

AD-A000 905 SYSTEMS RESEARCH LABS INC DAYTON OHIO RESEARCH APPLI--ETC P/O 11/6
MATERIALS EVALUATION. PART II. DEVELOPMENT OF CORROSION INHIBIT--ETC(U)
SEP 79 M KMOBAID F33615-76-C-8191
UNCLASSIFIED SRL-6909-02-PT-2 AFML-TR-79-6127-PT-2 NL

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AFML-TR-79-4127

Part II

MATERIAL EVALUATION: PART II - DEVELOPMENT OF CORROSION INHIBITORS

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SEPTEMBER 1979

TECHNICAL REPORT AFML-TR-79-4127, Part II
Final Report for Period August 1976 to July 1978

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER AFML TR-79-4127, Part II	2. GOVT ACCESSION NO. (19) TR-79-4127-PT-2	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) Materials Evaluation, Part II, Development of Corrosion Inhibitors	5. TYPE OF REPORT & PERIOD COVERED (9) Final Report Aug 1976 - July 1978	6. PERFORMING ORGANIZATION NUMBER 6909-02 Final	
7. AUTHOR(s) M. Khobaib, Ph.D.	8. CONTRACT OR GRANT NUMBER(s) (15) F33615-76-C-5191		
9. PERFORMING ORGANIZATION NAME AND ADDRESS Systems Research Laboratories, Inc. 2800 Indian Ripple Road Dayton, OH 45440	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS (16) 7351 (17) 73510690		
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Materials Laboratory AFML (LLN) Wright-Patterson Air Force Base, OH 45433	12. REPORT DATE (11) Sep 1979	13. NUMBER OF PAGES 63	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 655...	15. SECURITY CLASS. (of this report) UNCLASSIFIED	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) (14) SRL-6909-02-PT-2			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Inhibitors, anodic polarization, cathodic polarization, stress corrosion, corrosion fatigue, compact-tension plane-strain fracture-toughness specimens, pseudo-passivity, galvanic corrosion, crevice corrosion.			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A borax-nitrite based inhibitor has been developed for incorporation into the Air Force Rinse Facility at MacDill Air Force Base. Chromate-based products, in combination with polyphosphates, have been reasonably effective against corrosion of ferrous and nonferrous metals and alloys and are presently the most widely used inhibitors. However, the use of chromates has been the subject of ecological concern, and the investigation discussed herein involves alternatives to chromates. The performance of nonchromate commercial →			

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inhibitors has been tested and a borax-nitrite based formulation developed which inhibits the corrosion of several ferrous and nonferrous metals and alloys. This mixture contains no chromates and offers important advantages over the chromate-polyphosphate combination. Corrosion-fatigue and crack-growth studies on aluminum alloys have shown a reduction of more than one order of magnitude in crack-growth rate in the presence of this inhibitor. In fact, the crack growth decelerates to the air-sample level with the use of the inhibitor, even in an aqueous environment of 0.1M NaCl solution.

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FOREWORD

This report constitutes Part II of AFML-TR-79-4127 and was prepared by Dr. M. Khobaib, Research Applications Division, Systems Research Laboratories, Inc. (SRL), under Contract F33615-76-C-5191.

The Project Scientist monitoring this portion of the program was Dr. C. T. Lynch of the Air Force Materials Laboratory (AFML/LLN), Wright-Patterson Air Force Base, OH. This report covers work performed during the period August 1976 to July 1978 and was submitted by the author in July 1979.

This program was conducted in part at SRL, Dayton, OH, and in part at the Air Force Materials Laboratory at Wright-Patterson Air Force Base, OH, utilizing AFML mechanical-test facilities and some electrochemical-measurement equipment. The program was under the supervision of Dr. M. Khobaib. Mr. Carl Slife of SRL assisted in the compilation of the data. Part I of this report is entitled, "Mechanical Property Testing and Materials Evaluation and Modeling."

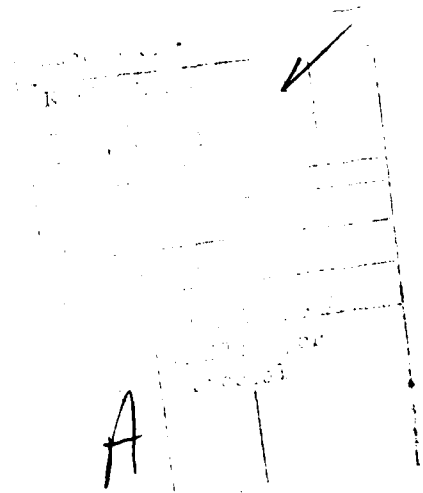


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SECTION I

INTRODUCTION

A recent study conducted by NBS has indicated that the cost of corrosion in the United States is approximately \$70 billion,¹ with the United States Air Force bearing more than \$1 billion of the burden. In order to minimize this cost, the Air Force has been searching for ways to combat corrosion in all its forms. Several years ago, a study² conducted by the United States Navy on corrosion prevention in carrier-based aircraft revealed that by merely rinsing the aircraft with water to remove detrimental particles such as salt and ash, a considerable savings could be realized in terms of corrosion maintenance. By late 1975, the USAF had made a decision to build a rinse facility for the F-4 aircraft and to install it under AFLC/WRALC and TAC at MacDill Air Force Base. At the corrosion managers conference at WRALC in the fall of 1975, questions concerning hard-water rinsing as opposed to inhibited- or demineralized-water rinsing were raised, and apparently Dr. C. T. Lynch of AFML was given the task of reviewing this problem. In rinsing aircraft, a very good possibility exists that water will be trapped in crevices or so-called dry-bay areas and that trapped hard water will cause serious corrosion problems and, hence, completely jeopardize the advantage of hard-water rinsing as a corrosion-control method. Therefore, incorporation of a low concentration of a nontoxic water-soluble inhibitor into the rinse facility was suggested. The Air Force Materials Laboratory decided to sponsor a research program for development of a water-soluble nontoxic inhibitor for incorporation into the Air Force Rinse Facility at MacDill Air Force Base in Tampa, Florida.

Although chromate-based^{3,4} corrosion inhibitors have been widely used to combat corrosion of ferrous and nonferrous metals and alloys, the use of chromates has recently been the subject of ecological concern. The investigation described herein was carried out to search for alternatives to chromates, one such alternative being a borax-nitrite based inhibitor. The value of borax nitrite as a corrosion inhibitor has long been recognized and studied.^{5,6} Earlier work at both SRL and AFML has shown a borax-nitrite combination to be very effective in controlling general

corrosion as well as crevice corrosion of high-strength steels.⁷ However, this combination was not found to be effective against the corrosion of other ferrous and nonferrous metals and alloys. The present study was concerned with the development of a nontoxic multifunctional corrosion inhibitor which would be effective against corrosion of ferrous and nonferrous metals and alloys. More than four hundred inhibitor compounds and formulations were surveyed with regard to their effect upon electrochemical behavior, general corrosion, galvanic corrosion, and crevice corrosion. As a result a borax-nitrite based inhibitor was developed and is currently being used in the Air Force Rinse Facility at MacDill Air Force Base. This mixture contains no chromate, is biodegradable, and offers important advantages over chromate-based combinations.

SECTION II

GENERAL BACKGROUND AND OBJECTIVES OF THE PROGRAM

Corrosion has become one of man's major economic and technical problems. A recent study conducted by NBS indicated that corrosion is costing the United States approximately 70 billion dollars annually.¹ The annual maintenance cost for military aircraft is several billion dollars. The costs directly associated with corrosion including repair and inspection of U.S. Air Force aircraft are at least 25% of the total maintenance cost.⁸

The fact that costs for both operation and maintenance are rising while procurement costs are remaining fairly constant prompted a major effort to reduce the cost of maintenance operations. Three approaches to minimizing these tremendous costs involve design of the product, selection of materials, and use of preventive anti-corrosion measures. Two common corrosion-prevention methods utilize protective coatings and inhibitors.

Several years ago, a study conducted by the U.S. Navy on corrosion prevention in carrier-based aircraft revealed that by merely rinsing the aircraft with water to remove detrimental particles such as salt and ash, a considerable savings could be realized in terms of corrosion maintenance.² By late 1975, the U.S. Air Force had made a decision to build a rinse facility for the F-4 aircraft and to install it under AFLC/WRALC and TAC at MacDill Air Force Base in Tampa, Florida. At the corrosion managers conference at WRALC in the fall of 1975, questions concerning hard-water rinsing as opposed to inhibited- or demineralized-water rinsing were raised. In rinsing aircraft, there is a good possibility that water will be trapped in crevices or so-called dry-bay areas and that trapped hard water will cause serious corrosion problems, completely jeopardizing any advantage which hard-water rinsing may have had as a corrosion-control method. Therefore, incorporation of a low concentration of a nontoxic water-soluble inhibitor into the rinse facility was suggested. This suggestion formed the basis for this project which deals with the development of a water-soluble nontoxic inhibitor to be incorporated into the rinse facility at MacDill Air Force Base. The main objective of the program was to determine

the effectiveness of corrosion inhibitors for use in aircraft rinse facilities and the compliance of these inhibitors with Federal and State environmental protection requirements. Since repair or replacement of corrosion-damaged parts on aircraft is extremely costly, prevention or retardation of corrosion rates should represent a considerable cost savings to the Air Force. The rinse facility at MacDill Air Force Base was chosen as the site for testing the effectiveness of adding corrosion inhibitors to rinse water.

Several commercial inhibitors are available for various service applications such as cooling-tower circuits, central heating systems, and automotive radiators. These formulations are normally combinations of several classes of inhibitor compounds, some functioning as anodic inhibitors and others as cathodic inhibitors. Commercial experience has shown that such combinations are often more effective due to some synergistic⁹ effect. Unfortunately, most of them are optimized for a specific application. The results of work conducted at AFML have demonstrated an encouraging inhibition effect of borax nitrite upon high-strength steels;¹⁰ chromates have not been found to be so effective in the presence of chloride ions.¹¹ The promising results of the borax-nitrite combination were observed in crack-growth experiments--both in static tests and cyclic corrosion-fatigue tests. However, this combination itself was not effective in inhibiting the corrosion of high-strength aluminum alloys, copper, and other alloys used in aircraft structures. But the encouraging results obtained on high-strength steels served as the basis for further exploration.

SECTION III EXPERIMENTAL

1. PROGRAM OVERVIEW

A very extensive research program was conducted to survey and screen most of the commercially available inhibitors in an attempt to determine their suitability and compatibility with rinse water. A major effort was simultaneously undertaken to develop a water-soluble nontoxic inhibitor to be used in case the commercially available inhibitors were incompatible.

The research was divided into four phases. In Phase I of the program, background data were collected and a list of suitable candidates for inhibitor combinations formulated. The variables considered in the selection of inhibitors are given in Table I. The promising inhibitor candidates were selected from the generic types shown in Table II. More than four hundred candidate materials were considered. Table III gives the names of some of the commercially available inhibitors which were also included in the final selection process. During formulation of the inhibitor combination, special attention was given to the fact that the resulting formulations must be compatible with EPA and state laws governing ground-water discharge and sewage-disposal discharge. During this time, analysis of the water at MacDill Air Force Base in Tampa, Florida, was being conducted routinely on a monthly basis. A sample analysis is shown in Table IV. Concurrently with the main effort of Phase I, specimens were fabricated for the immersion testing and stress-corrosion and corrosion-fatigue experiments to be carried out in Phases II and III.

Phase II consisted mainly of electrochemical characterization of the candidate alloys. In addition to the different types of polarization tests, immersion tests were also conducted, followed by visual observation, to determine the effectiveness of inhibitors against corrosion.

In Phase III, low-cycle-fatigue tests were conducted to determine the effectiveness of inhibitor combinations selected from Phase II against the environmental enhancement of fatigue cracks. Static sustained-load tests for

TABLE I
INHIBITORS - GENERAL CONSIDERATIONS

Multifunctional Inhibitors

Cathodic

Anodic

Chloride Absorbers

Buffers

Solubility Range

Influence Upon Hydrogen Entry Rates

Toxicity

TABLE II
INHIBITORS - COMPOUNDS

<u>Cathodic</u>	Polyphosphate Zinc Silicate
<u>Anodic</u>	Orthophosphate Chromate Ferrocyanide Nitrite
<u>Combinations</u>	Polyphosphate-Chromate Polyphosphate-Ferrocyanide Borax-Nitrite Fluoride-Chromate Benzoate-Nitrite Silicate-Chromate
<u>Film Formers</u>	Emulsified or Soluble Oils Octadecylamine Long-Chain Amines Alcohols and Carboxylic Acids

TABLE III
LIST OF SOME COMMERCIALY AVAILABLE INHIBITORS

<u>Inhibitor</u>	<u>Manufacturer</u>
Nalco 39L	Nalco
Nalco 41L	
Nalco 918	
Nalco 26W	
Etc.	
Dequest	Monsanto
Betz 545	Betz Lab
Calgosil	Calgon
CS	
Virco Pet 30	Mobil

TABLE IV

CITY OF TAMPA - WATER DEPARTMENT
AVERAGE DAILY ANALYSIS OF FINISHED WATER
JUNE 1977

	<u>Color</u> Units	<u>Total</u> <u>Hardness</u> CaCO ₃	<u>Total</u> <u>Alkalinity</u> CaCO ₃	<u>Calcium</u> <u>Hardness</u> CaCO ₃	<u>pH</u> Units	<u>Residual</u> <u>Chlorine</u>	<u>Temp</u> °F
Maximum	4	196	118	164	7.6	3.5	81
Minimum	3	171	103	142	7.4	2.7	77
AVERAGE	3	181	110	154	7.5	3.2	79

JUNE MONTHLY COMPOSITE
COMPLETE ANALYSIS

(Results expressed in milligrams per liter)

Calcium	Ca	61.60
Magnesium	Mg	7.00
Sulfates	SO ₄	55.00
Chlorides	Cl	57.00
Fluorides	F	0.32
Sodium	Na	36.00
Potassium	K	3.20
Nitrates	NO ₃	0.08
Silica	SiO ₂	4.40
Manganese	Mn	0.00
Iron	Fe	0.08
Bicarbonates	HCO ₃	136.00
Phosphates	PO ₄	0.26
Aluminum	Al	0.30
Total Solids		350.00
Total Hardness	CaCO ₃	180.00
Total Alkalinity	CaCO ₃	112.00
Non-Carbonate Hardness	CaCO ₃	68.00
Ammonia-Nitrogen	NH ₃	ND
L.A.S.	MBAS	0.03
Copper	Cu	0.03
Color	Units	3.00
Turbidity	Units	0.70
pH	Units	7.60
Temperature	°F	76.00
Specific Conductivity	MMhos	425.00
B.O.D. (5 days at 20°C)		0.20

stress-corrosion cracking were also conducted to determine possible enhancement of K_{ISCC} (threshold stress intensity) through incorporation of the inhibitor.

More electrochemical tests were conducted in Phase IV. The inhibitor formulation was then optimized with respect to the effect of chloride-ion content in water. The formulation was finalized and custom blending and packaging was negotiated with a local company in Tampa, Florida.

Nearly three thousand pounds of the inhibitor were bought over a six-month period. Arrangements were made with Mr. Mike Cawley for SRL to supervise and aid in the incorporation of the inhibitor into the rinse facility. Performance was monitored for several months, and very satisfactory results were obtained during these operations.

2. PHASE I - DATA COLLECTION, MATERIAL ACQUISITION, AND PRELIMINARY ANALYSIS

Major firms dealing with inhibitors were contacted, and commercially available inhibitor samples were collected along with detailed literature on toxicity, biodegradability, etc. The screening of the inhibitors from the generic types shown in Table II was a complex process. The toxicity consideration was given the highest priority in the screening process. If an inhibitor species was obviously toxic based upon data in the literature,¹² it was eliminated from further consideration. Chromates, molybdates, and aniline additions are some examples of inhibitors which were eliminated on these grounds. However, some constraint was exercised since almost all materials might conceivably be toxic under special circumstances. Specific guidelines on toxicity were not available; therefore, qualitative judgments were made in assessing relative toxicity.

A detailed chemical analysis of Tampa water was obtained every month. A sample is shown in Table IV. High-strength aluminum alloys such as 2024-T3 and 7075-T6 and high-strength steel such as 4340 with yield strength near 200 ksi were chosen as testing materials and were obtained from a local supplier. Standard specimens for immersion, electrochemical, stress-corrosion, and corrosion-fatigue tests were fabricated for use in Phases II and III.

3. PHASE II - DETERMINATION OF EFFECTIVENESS OF INHIBITOR-SYSTEMS

The determination of effectiveness of inhibitor systems was an involved process due to the large number of possible compatible inhibitors. Initially it was difficult to trace the source of a commercially available inhibitor. More difficult and time consuming was the screening process for the possibly vast number of combinations obtainable through Table II.

The anodic-cathodic combination, in general, is capable of inhibiting either corrosion process which occurs locally on the structure. At the same time, polarization is more effective with a mixture of anodic and cathodic than with either separately. The situation is quite complex because either inhibitor may vary in concentration from several parts per million up to a few percent; and, in general, a narrow band of composition exists within which the optimum can be obtained. In addition, the synergistic effect of several other ingredients such as the film former, chloride absorber, and chelating agents was determined. These ingredients together constituted a massive number of formulations to be tested. Overall more than 400 combinations were tested. An alternative was to screen the commercially available inhibitors which claimed to be effective and compatible with rinse water. With this view in mind, inhibitor samples were obtained from Monsanto, Nalco, Betz Lab, Calgon, etc. The problem of evaluation and development of an inhibitor which would be compatible with the rinse facility was attacked simultaneously. The commercial inhibitors were evaluated by the fool-proof standard method of immersion.

a. Immersion Tests

Immersion tests with more than 400 different mixtures (potential inhibitors) were conducted. Selected results and inhibitor-performance data are shown in Table V. Several of these mixtures are commercially available inhibitors used for corrosion protection of ferrous and nonferrous metals, while others were formulated from the literature¹⁰⁻¹⁵ and experience gained during the testing.

Very systematic immersion tests were carried out on high-strength aluminum alloys (2024-T3 and 7076-T6) high-strength 4340 steel, copper, cast iron,

TABLE V

IMMERSION TEST RESULTS

No. of Tests	Electrolyte	pH		Surface Appearance (Visual Observation)		Corrosion Rate (mpy)		Remarks
		Initial	Final	2024-T3	7075-T6	2024-T3	7075-T6	
1 5	Tap Water (WPAFB)	7.62	8.48	Stained; several pits.	Couple of oxide patches; several pits.	0.034 to 0.65	0.38 to 0.78	Should be inhibited.
2 5	Distilled Water	6.98	7.80	Entire surface attacked; lack of deep pitting.	Entire surface attacked; lack of deep pitting.	0.34 to 0.57	0.051 to 0.95	Should be inhibited.
3 5	0.1M NaCl in Distilled Water	6.95	7.50	Entire surface attacked; several pits.	Entire surface attacked; several pits.	1.38 to 1.98	1.54 to 2.4	Should be inhibited.
4 2	20% NaCl in Distilled Water	7.10	7.45	Entire surface attacked; several pits.	Entire surface attacked; several pits.	0.63 to 1.01	1.10 to 1.34	Should be inhibited.
5 3	0.035M (Sodium Borate + Sodium Nitrite) in Tap Water	8.95	8.90	Couple of dark patches; the other area lightly tinted.	Light tinted oxide all over.	0.071 to 0.23	0.31 to 0.51	Very poor inhibition.
6 3	NALCO 39L (18cc/liter) in Tap Water	9.24	9.00	Looks as original. Deposit at the bottom.	0-1% Deposit at the bottom.	$< 10^{-4}$	$< 10^{-4}$	Very good.
7 3	NALCO 41 (18 cc/liter) in Tap Water	7.14	6.98	Clean as original.	Couple of oily patches; otherwise, clean.	$< 10^{-4}$	$< 10^{-4}$	Good.

TABLE V (Cont'd)

IMMERSION TEST RESULTS

No. of Tests	Electrolyte	pH		Surface Appearance (Visual Observation)		Corrosion Rate (mpy)		Remarks
		Initial	Final	2024-T3	7075-T6	2024-T3	7075-T6	
8	3 NALCO 26W (20 ppm) in Tap Water	9.05	8.92	Surface clean; several pea-size pits.	Entire surface attacked; shallower pits.	0.22 to 0.81	0.18 to 0.87	Very poor.
9	3 NALCO 918 (20 ppm) in Tap Water	8.62	8.46	Pits all over.	Pits all over.	0.34 to 0.96	0.38 to 0.74	Very poor
10	3 Betz 545 (500 ppm) in Tap Water	8.83	8.42	Corners and edges badly pitted; surface fairly clean.	Entire surface dark; several pits.	0.017 to 0.063	0.028 to 0.054	Poor.
11	2 Calgosil (2000 ppm) in Tap Water	8.50	8.40	Slightly dark scale all over; no visible pits.		0.010 to 0.18	0.13 to 0.15	Very poor.
12	2 Calgon Inhibitor CS (4000 ppm) in Tap Water	8.90	8.80	Light tinted scale all over; no visible pits.		0.067 to 0.088	0.083 to 0.092	Poor.
13	1 1% Sodium Dichromate in Tap Water	5.80	5.80	Surface looks as original.		$< 10^{-4}$	$< 10^{-4}$	Very good.
14	3 0.1% (Sodium Metasilicate + Sodium Polyphosphate) in Tap Water.	8.64	8.45	Surface looks as original; lot of residue at the bottom.		$< 10^{-4}$	$< 10^{-4}$	Very good.

TABLE V (Cont'd)

IMMERSION TEST RESULTS

No.	No. of Tests	Electrolyte	pH		Surface Appearance (Visual Observation)		Corrosion Rate (mpy)		Remarks
			Initial	Final	2024-T3	7075-T6	2024-T3	7075-T6	
15	3	0.035M (Sodium Borate + Sodium Nitrite) in Tap Water	8.95	8.90	Couple of dark patches; lightly tinted.	Light tinted oxide all over.	0.071 to 0.23	0.31 to 0.51	Very poor.
16	10	0.5% Sodium Borate + 0.05% (Sodium Nitrite + Sodium Nitrate) + 0.003% (Sodium Polyphosphate + Sodium Metasilicate) + 10 MBT in Tap Water	8.78	8.84	Surface looks as original.		$< 10^{-4}$	$< 10^{-4}$	Excellent.

TABLE V (Cont'd)
IMMERSION TEST RESULTS ON GALVANICALLY COUPLED SAMPLES

Specimen	Inhibitor	pH		Surface Appearance (Visual Observation)	Corrosion Rate (mpy)	Remarks
		Initial	Final			
2024-T3	0.35 Borate + 0.05	8.98	9.05	Surface as original.	$< 10^{-4}$	Excellent.
	Nitrite + 0.05					
	Nitrate + 0.003					
	Silicate + 0.003					
	Phosphate + 10 MBT					
7075-T6	"	8.98	9.05	Surface as original.	$< 10^{-4}$	Excellent.
4340 Steel	"	8.98	9.05	Surface as original.	$< 10^{-4}$	Excellent.
Cast Iron	"	8.98	9.05	Surface as original.	$< 10^{-4}$	Excellent.
Brass	"	8.98	9.05	Surface as original.	$< 10^{-4}$	Excellent.
Copper	"	8.98	9.05	Surface as original.	$< 10^{-4}$	Excellent.

and brass. Standard 60 × 30 × 3.125 mm (4 × 2 × 1/8 in.) test coupons were used for immersion tests on aluminum alloys. Smaller coupons measuring 75 × 25 × 3.125 mm (3 × 1 × 1/8 in.) were used for high-strength steel, copper, cast iron, and brass. The specimen surface and pH of the electrolyte were checked periodically. After an immersion period of 1000 hr, the specimens were removed from the solution. In some cases, specimens were exposed over a six-month period. Each specimen was inspected very carefully for discoloration, roughening, general corrosion, corrosion products, and size and location of pits. Then the specimens were cleaned in a solution of 2% chromic acid + 5% phosphoric acid at 80°C (175°F) for a period of 5-25 min., depending upon the thickness of the corrosion products. The weight loss measured for each specimen was converted to mpy (mils per year) according to

$$\text{mpy} = \frac{534W}{DAT}$$

where W = weight loss (mg)

D = density of specimen (gm/cm³)

A = area of specimen (sq. in.)

T = exposure time (hr).

In some cases, pieces of aluminum, high-strength steels, copper, brass, and cast iron were suspended together in one electrolyte to check the effectiveness of the inhibitors against interfering ions. Finally, the effectiveness of the inhibitor for metallic parts prone to galvanically coupled conditions was also examined. A galvanic couple was prepared as shown in Fig. 1. Pieces of aluminum, copper, brass, and steel sheet were connected through a stainless-steel rod and individually bolted with stainless-steel nuts. The results of these tests are also included in Table I.

b. Polarization Measurements

Since immersion tests are time consuming and it was almost impossible to carry out such tests on a massive number of possible formulations in the limited time frame, screening of the inhibitors was assisted by fast



Figure 1. Galvanic couple

and more refined techniques such as anodic, cathodic, and linear polarization. All tests were carried out in accordance with ASTM Standard G5-72, "Standard Recommended Practice For Standard Reference Method For Making Potentiostatic and Potentiodynamic Polarization Measurements." The measurements were conducted by means of an automated PAR unit consisting of a corrosion cell, potentiostat/galvanostat, log converter, programmer, and X-Y recorder. The experimental arrangement is shown in Fig. 2.

4. PHASE III - STRESS-CORROSION AND CORROSION-FATIGUE TESTS

Sustained-load stress-corrosion cracking and low-cycle corrosion-fatigue tests were conducted to determine the effectiveness of the inhibitor formulations in these situations. Compact-tension plane-strain fracture-toughness specimens (high-strength steels such as 4340 and HP17 and aluminum alloys of series 2000 and 7000 in T3, T6, and T73 in both LT and ST orientations) as shown in Fig. 3 were used to determine the crack-growth rate in various aqueous environments. A detailed description of the corrosion-fatigue tests on high-strength steels is included in Ref. 16.

Sinusoidal tension-tension cycling was used at a frequency of 0.1 Hz. All tests were performed at a maximum load of 545 kg (1200 lbs.) [except in the case of Piperazine solution where the maximum load was 816 kg (1800 lbs.)] and a stress ratio, $R (\sigma_{\min}/\sigma_{\max})$, of 0.1. The specimens were initially precracked to a fatigue-crack length of ~ 2.54 mm (0.10 in.). The crack length was monitored using a double-cantilever-beam gauge and an amplifier-recorder system. The crack-opening displacement (COD) was recorded as a function of fatigue cycles.

In order to determine the crack lengths from COD data, compliance measurements were carried out for all aluminum alloys. Tests were conducted in air, and crack lengths were determined using optical and COD measurements simultaneously on the MTS machine. No significant differences were observed in the COD/load-vs-crack length curves. The compliance curve was calculated using the least-squares curve-fit method which yielded crack lengths in millimeters from the COD values through the polynomial equation

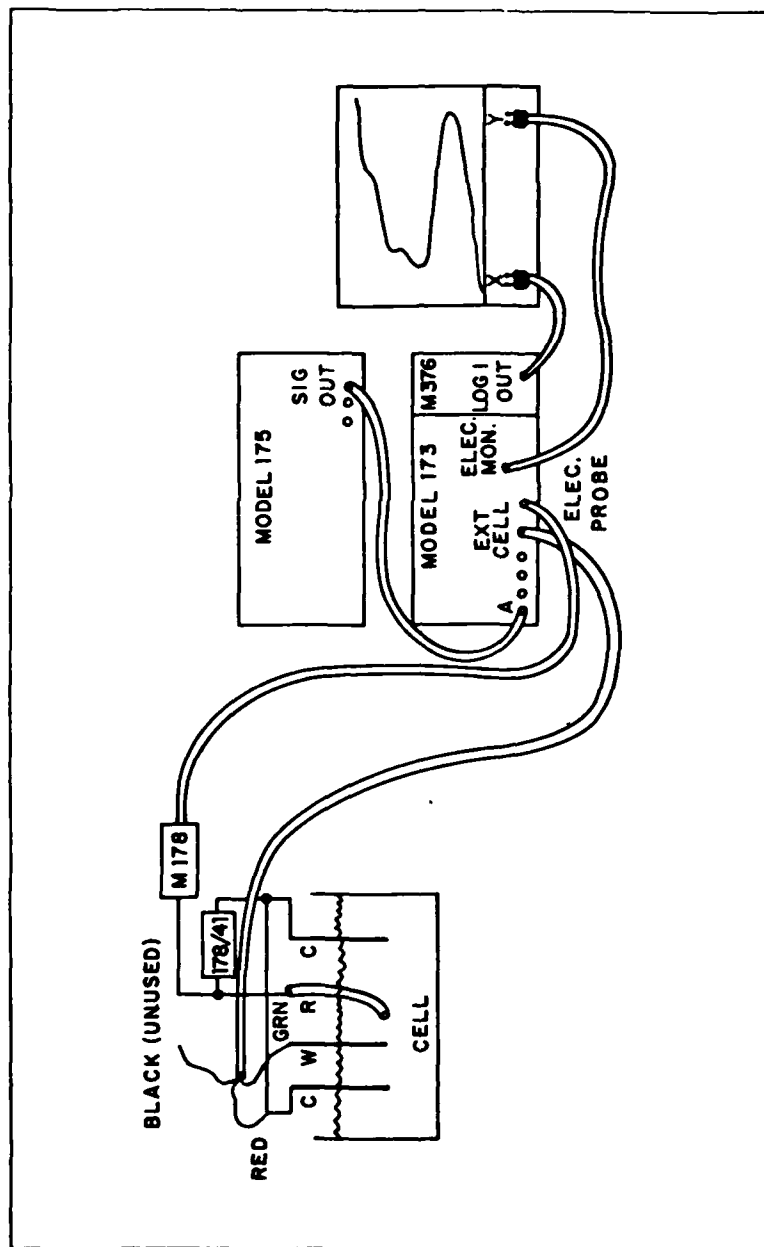


Figure 2. Test setup for corrosion measurements

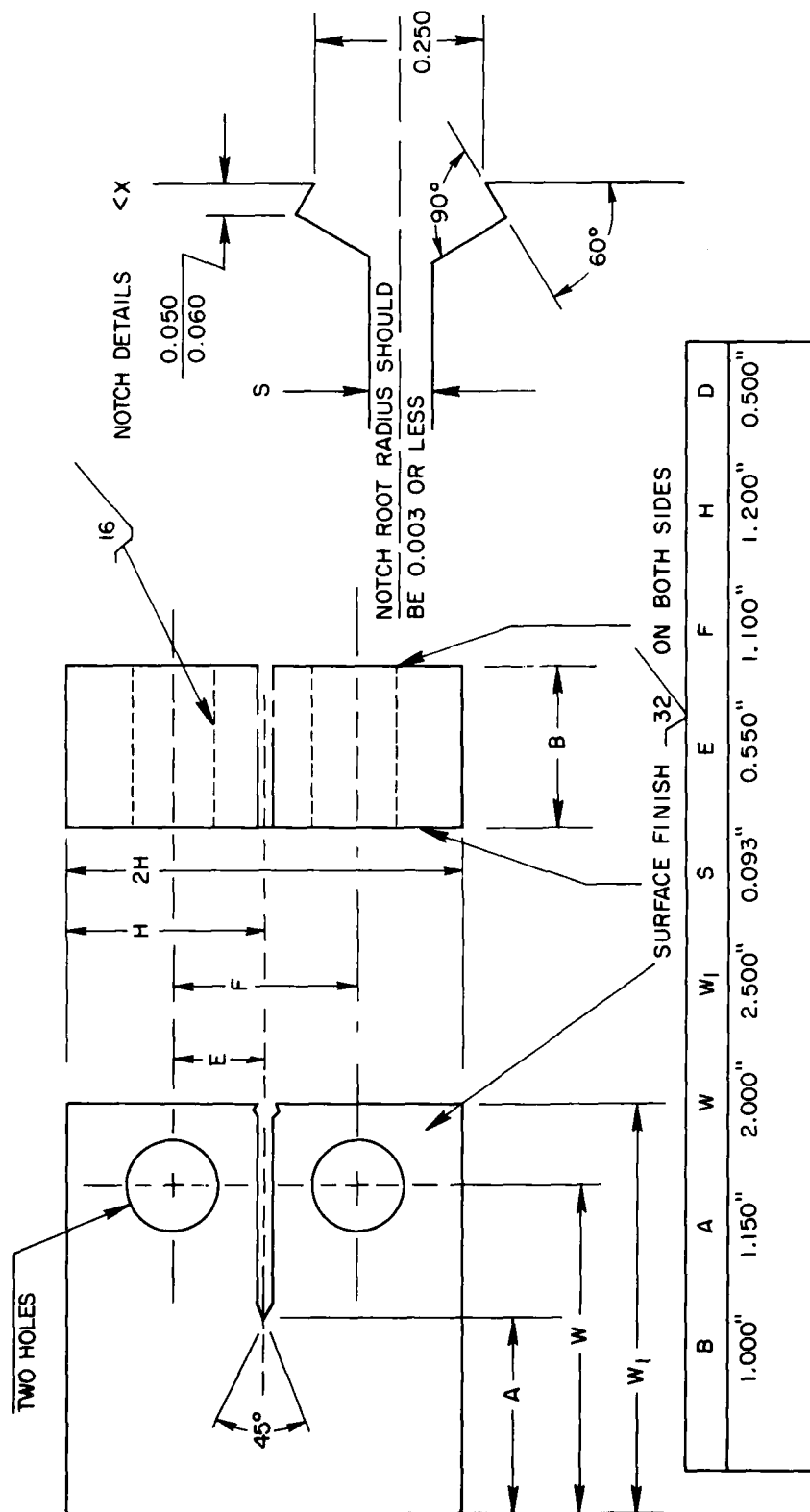


Figure 3. Plane-strain fracture-toughness specimen

$a = -0.104705 + 2.15785X - 1.27008X^2 + 0.360709X^3 - 0.0395174X^4$, where X is COD/load in (mils/kg) $\times 134$, and a is the crack length. The factor 134 is the mechanical advantage of the static test frames and is included to permit use of the same polynomial for both static and fatigue experiments. Using the crack-growth length, a, and the load, P, the stress-intensity values were calculated from¹³

$$K_1 = \frac{P}{BW^{1/2}} \left[29.6 \left(\frac{a}{W} \right)^{1/2} - 185.5 \left(\frac{a}{W} \right)^{3/2} + 655.7 \left(\frac{a}{W} \right)^{5/2} - 1017.0 \left(\frac{a}{W} \right)^{7/2} + 638.9 \left(\frac{a}{W} \right)^{9/2} \right]$$

where B and W are the dimensions indicated in Fig. 3, with B and a being greater than $(K_{IC}/Y_s)^2$, K_{IC} is the fracture toughness, and Y_s is the tensile yield strength. Computer programs were used to calculate and plot da/dt vs K and da/dN vs K. After mechanical testing, all fractured specimens were transferred to desiccators for subsequent chemical and fractographic analysis.

All fractured surfaces were carefully examined visually and then by light microscopy. The fracture surface was ultrasonically cleaned in acetone, deionized water, and methyl alcohol. The light-microscopic observation was followed by scanning electron microscopy (SEM) to permit a more detailed investigation. A 200-300 Å layer of gold was evaporated under vacuum onto the fracture surfaces to improve observation conditions in the SEM. Some of the samples had to be viewed at a 45° tilt to the incident beam, with the direction of crack propagation being toward the detector for better resolution. The crack-growth characteristics of the various alloy-environment systems are included in Figs. 4-12, and the fractographs are shown in Figs. 13-17.

5. PHASE IV - SELECTION OF INHIBITOR AND APPLICATION TO RINSE FACILITY

The main objective of the program was incorporation of a nontoxic water-soluble inhibitor into the rinse facility at MacDill Air Force Base, Tampa, Florida. Along with the continuing laboratory research work, a trip

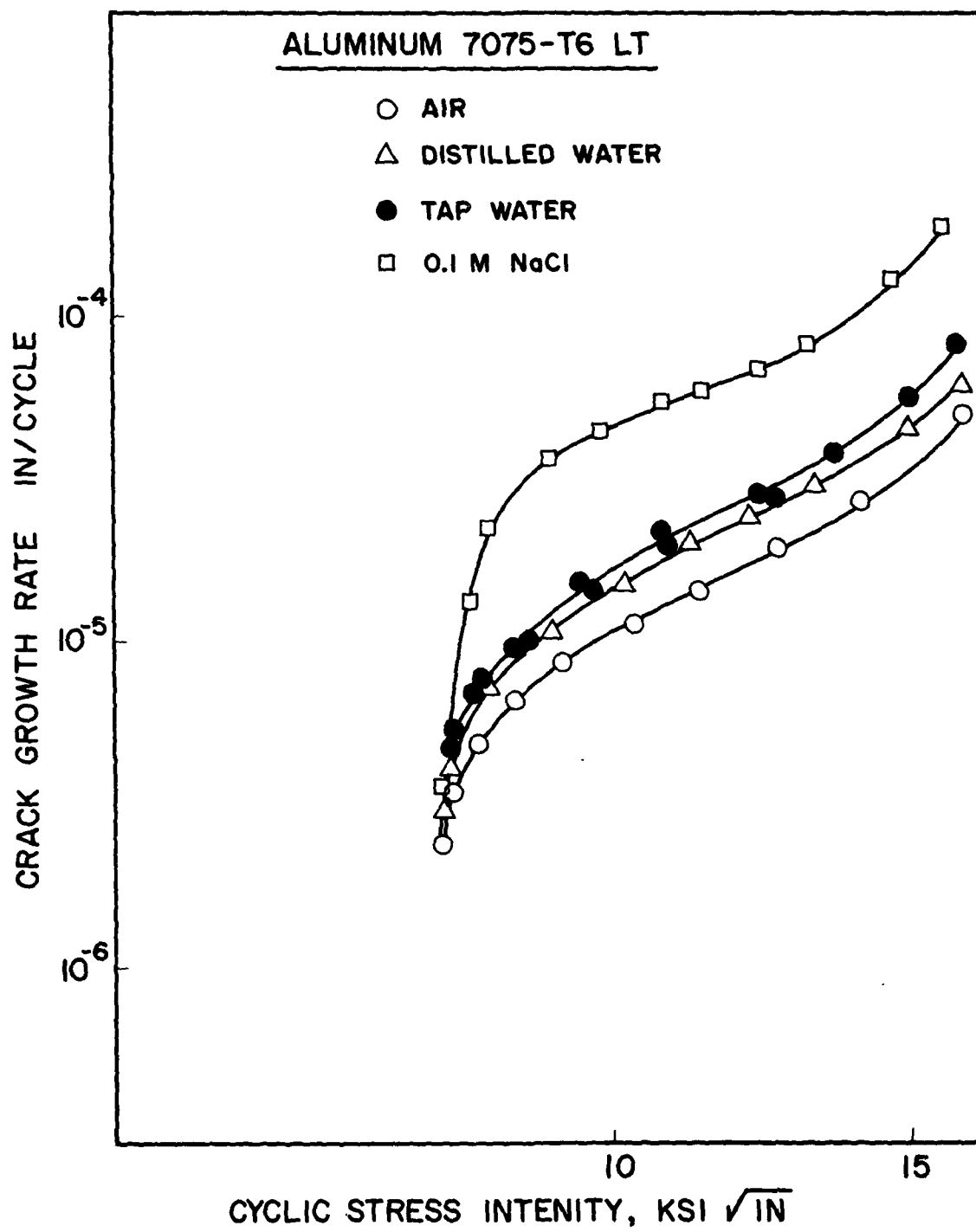


Figure 4. Corrosion fatigue of Al 7075-T6 LT

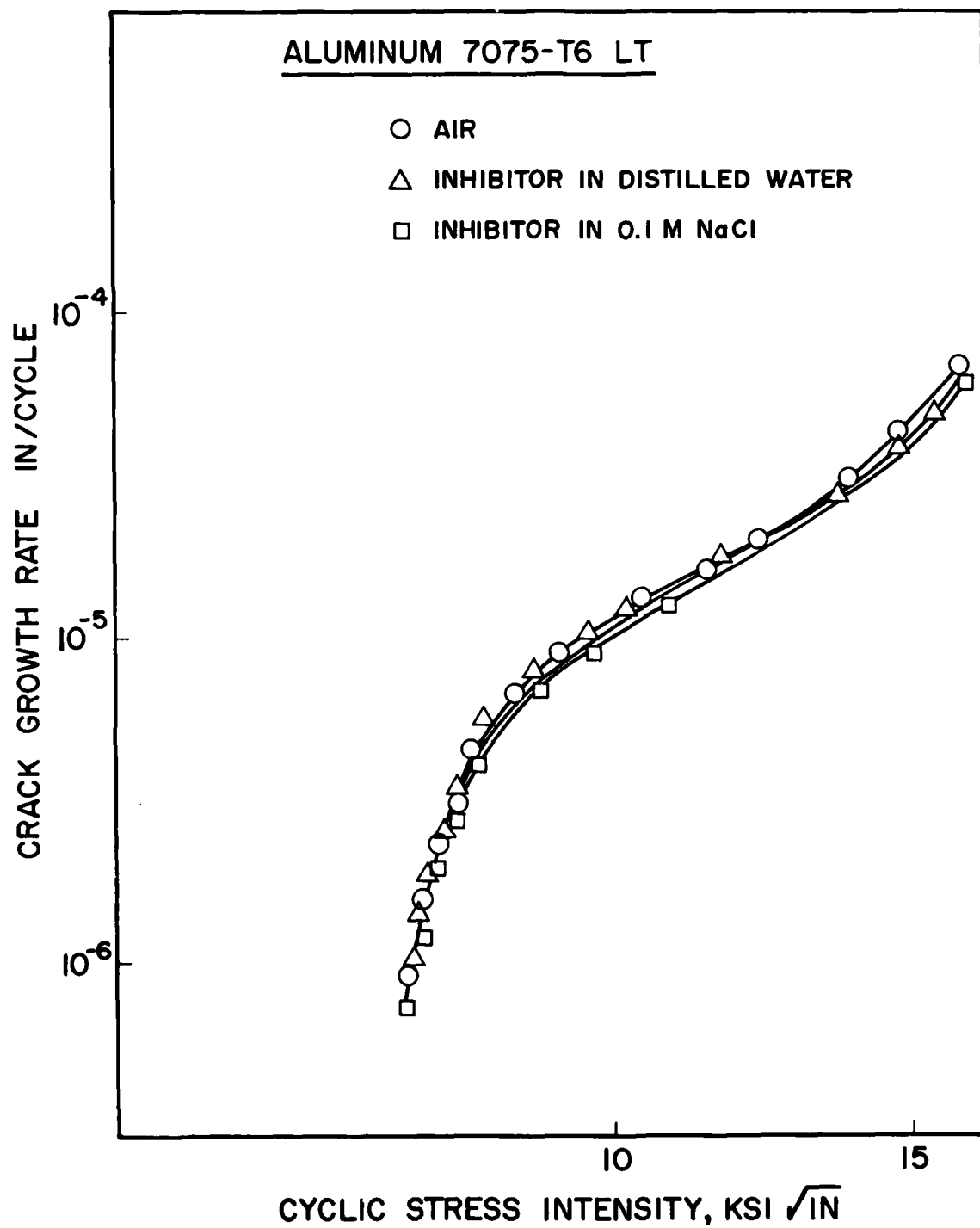


Figure 5. Effect of inhibitor upon corrosion fatigue of Al 7075-T6 LT

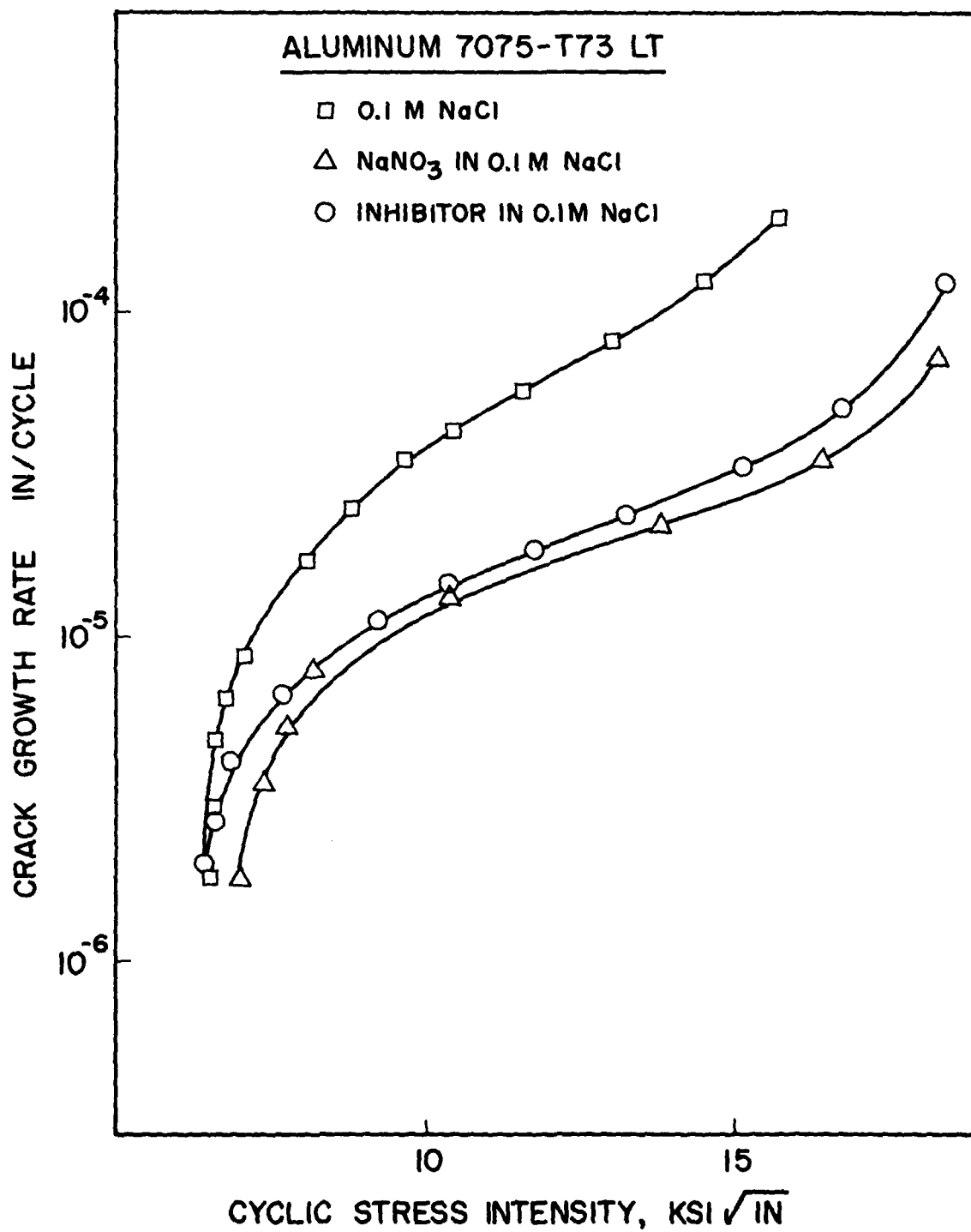


Figure 6. Corrosion fatigue of Al 7075-T73 LT

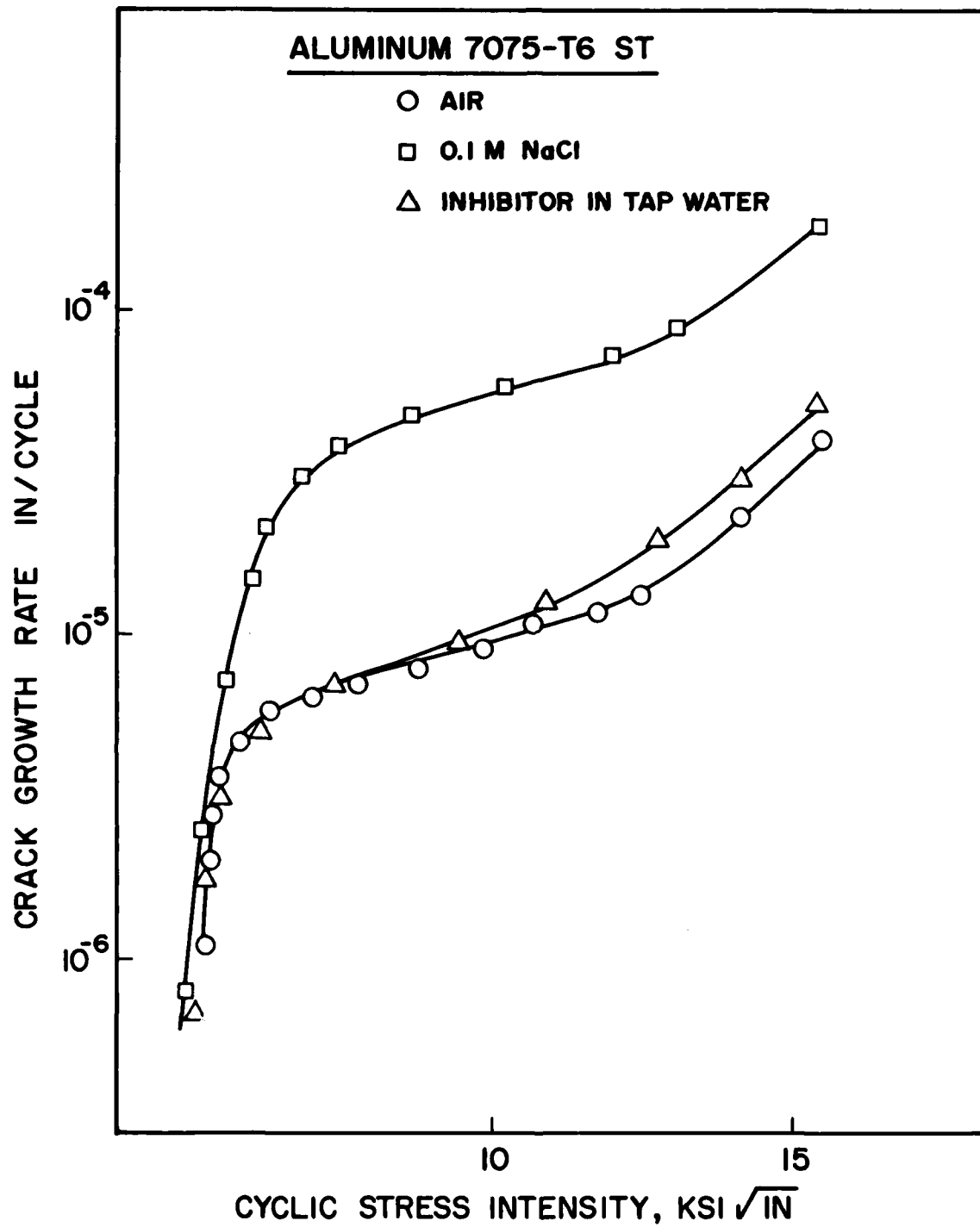


Figure 7. Corrosion fatigue of Al 7075-T6 ST

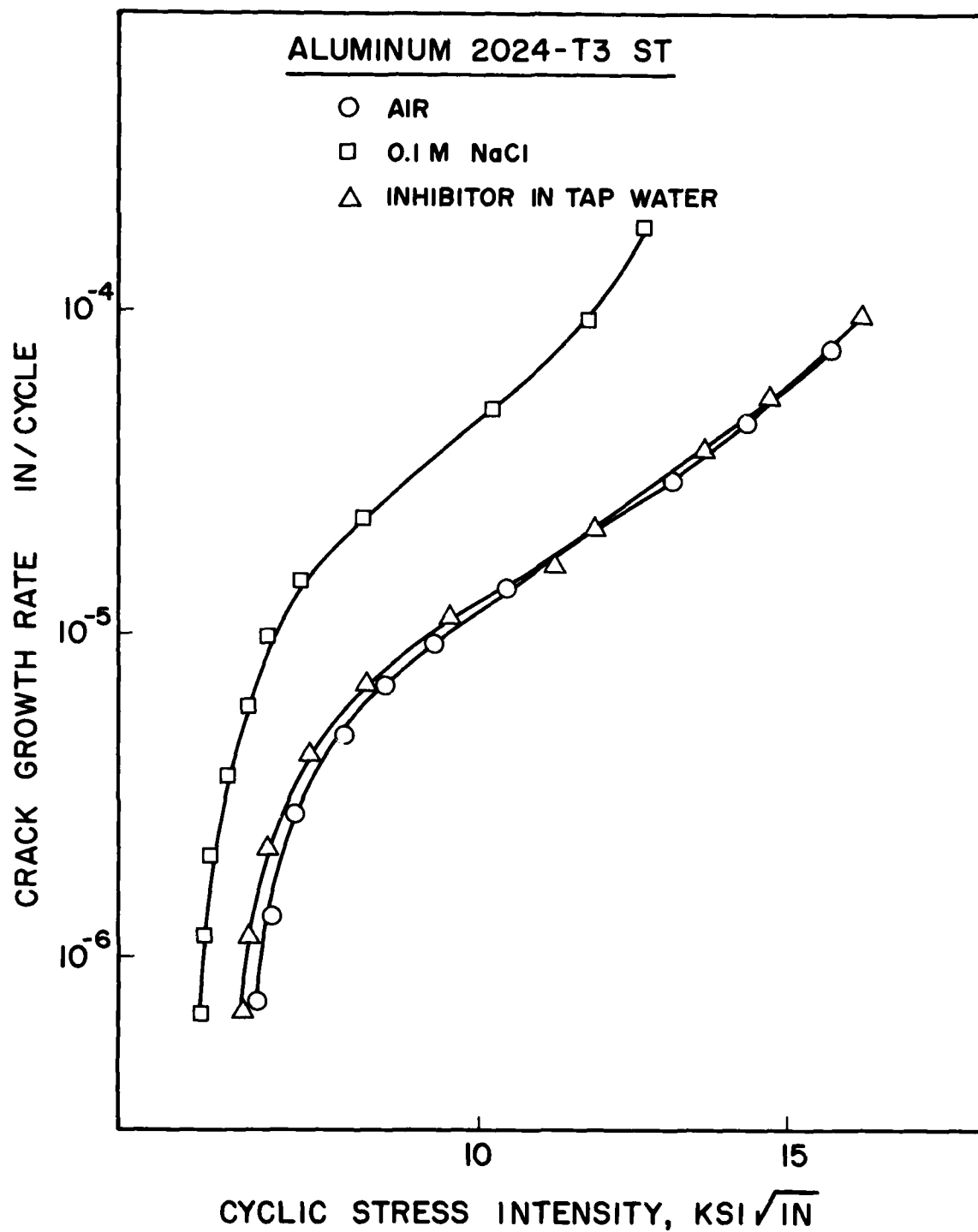


Figure 8. Corrosion fatigue of Al 2024-T3 ST

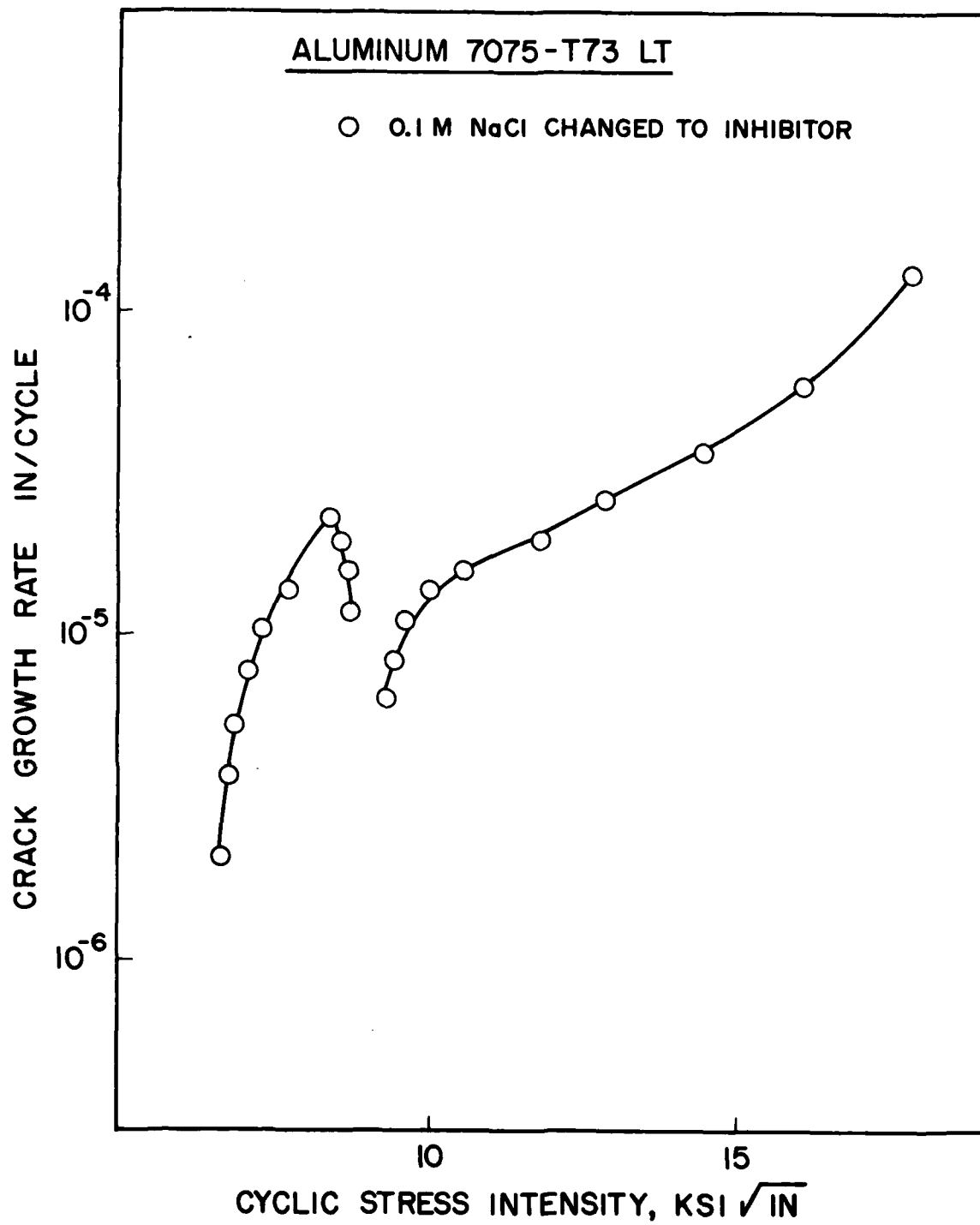


Figure 9. Crack-growth rate in sodium chloride replaced by inhibitor for Al 7075-T73 LT

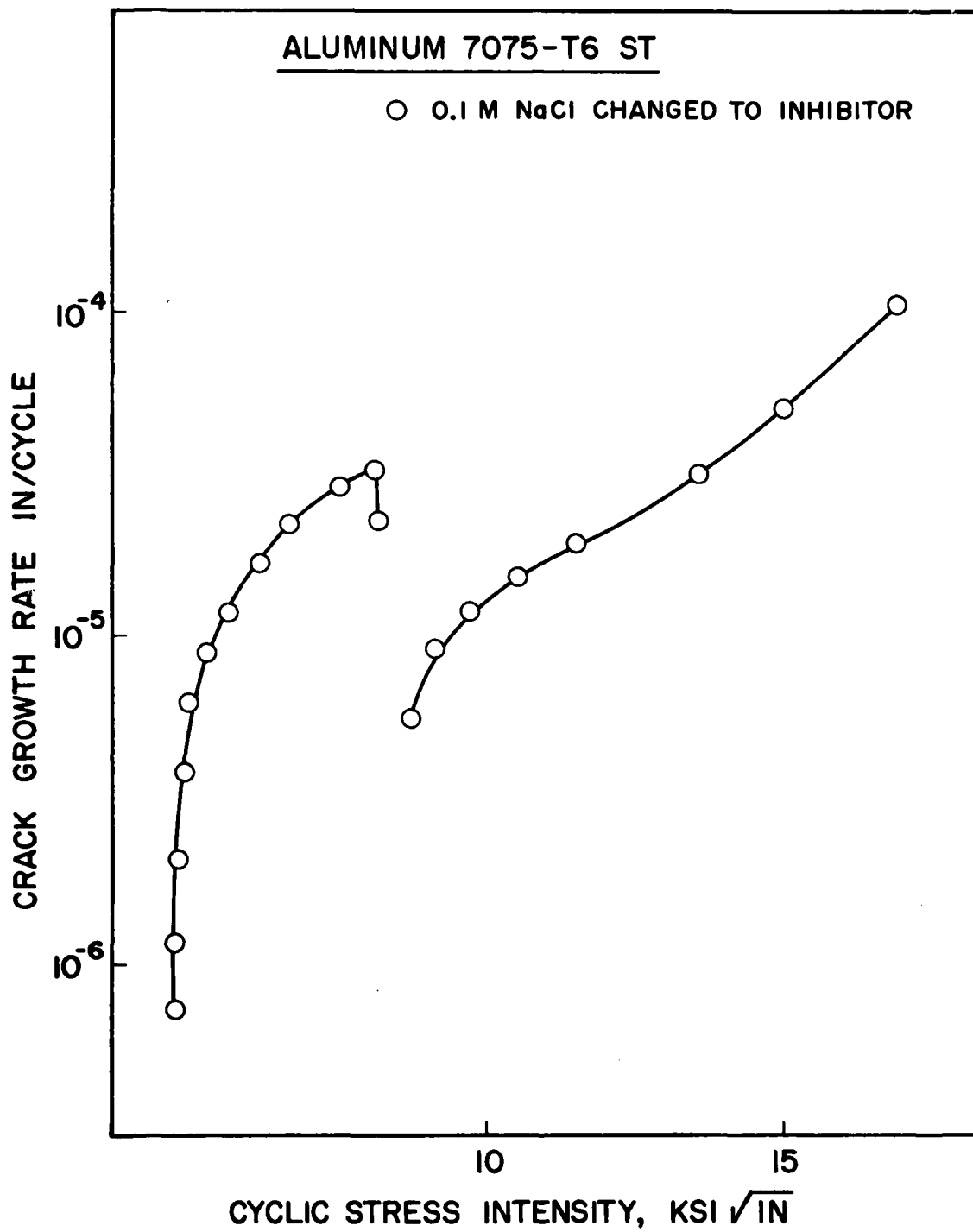


Figure 10. Crack-growth rate in sodium chloride replaced by inhibitor for Al 7075-T6 ST

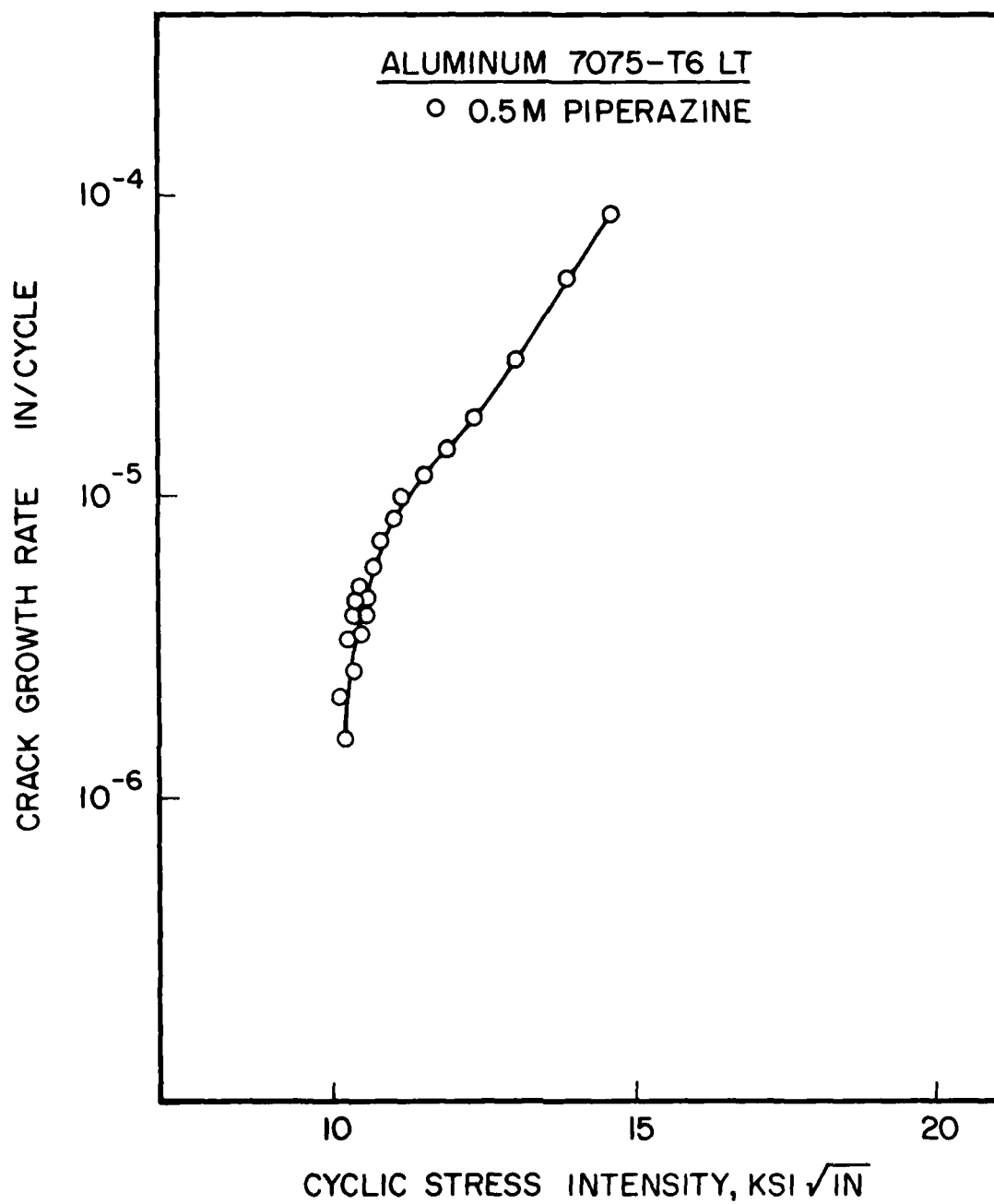


Figure 11. Corrosion fatigue in 0.5M Piperazine

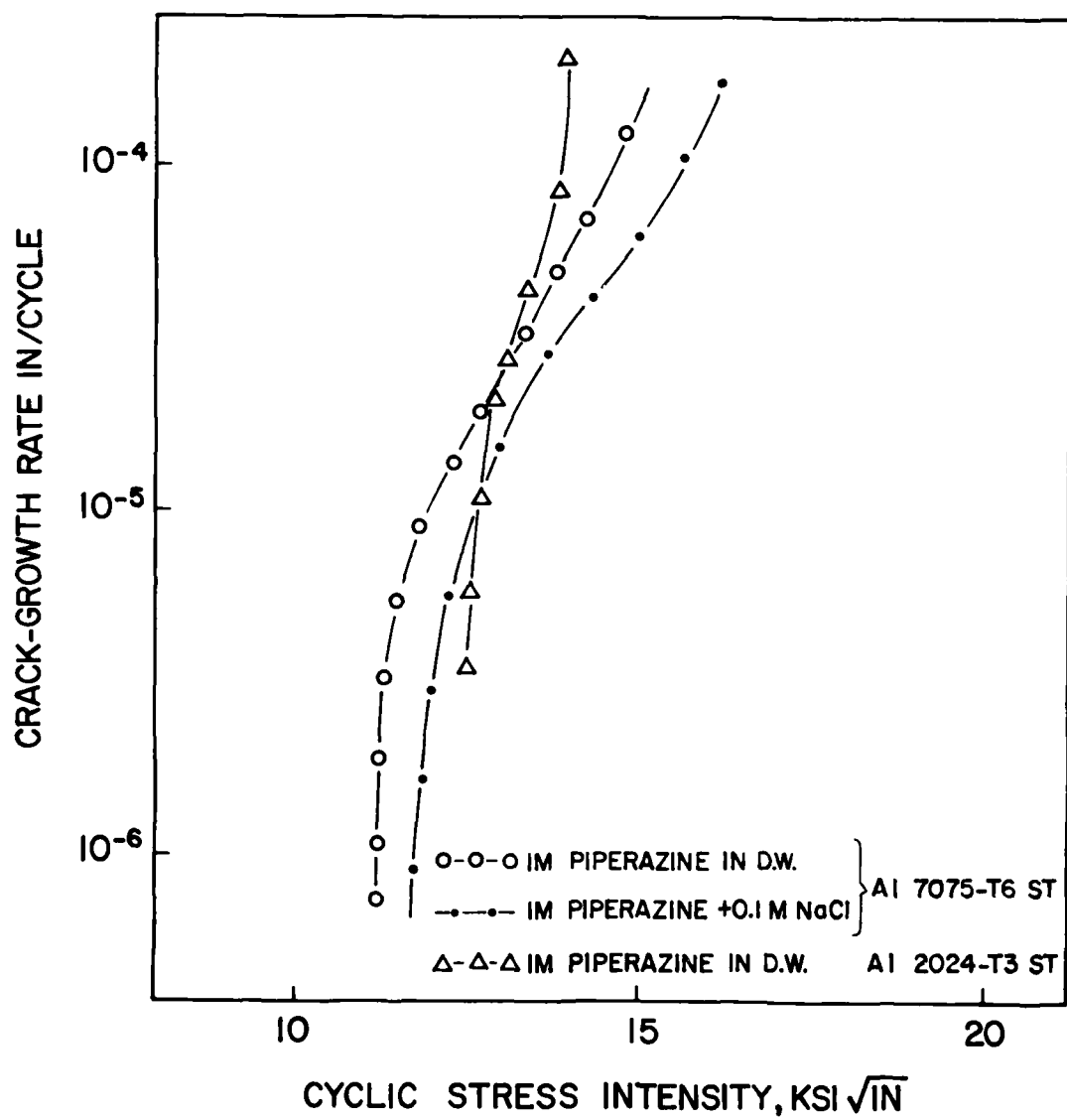


Figure 12. Corrosion fatigue in 1M Piperazine



Figure 13. Fracture surface of Al 7075-T6 alloy tested in air

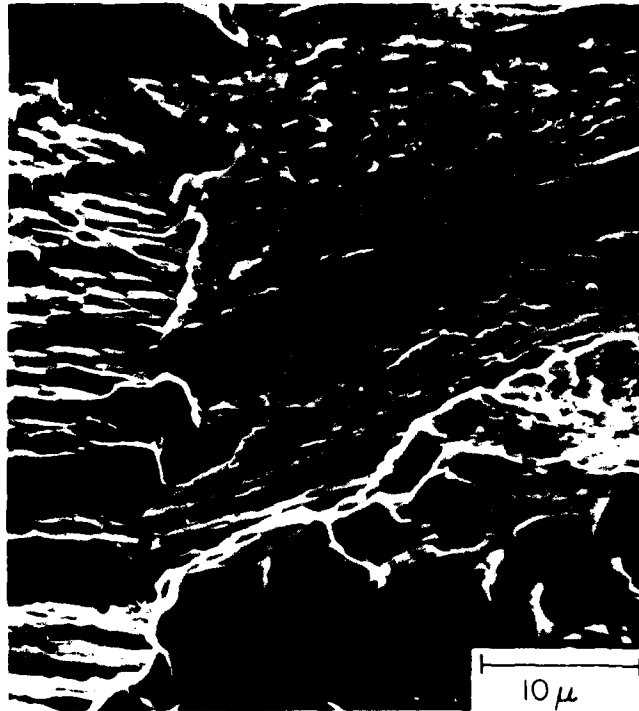


Figure 14. Fracture surface of Al 7075-T73 alloy tested in 0.1M NaCl



Figure 15. Fracture surface showing slip and fatigue striation



Figure 16. Fracture surface of Al 7075-T6 alloy tested in inhibitor solution



Figure 17. Fracture surface of Al 7075-T6 ST showing the transition from brittle to ductile morphology

was made to MacDill in mid-September of 1977 to observe the performance of the rinse facility and determine the feasibility of the incorporation of an inhibitor into the rinse-water system. The detailed operation of the facility and the possibility of either continuous or batch feeding of the inhibitor into the rinse-water tank were discussed with Mr. Mike Cawley at the rinse facility at MacDill. It was concluded that arrangements will be required for automatic control of the inhibitor concentration in the rinse tank based upon conductivity, turbidity, or some concentration measurement.

The rinse-water facility was in operation and F-4's were being washed with uninhibited water to test the operation of the facility and provide some experience for modification. Figure 18 shows one of the F-4's going through the facility. Samples of (a) fresh water going into the tank, (b) water collected immediately after rinsing of the airplane, and (c) water from the storage tank which contains a mixture of fresh water and water from several rinses were collected and brought back to the laboratory for the purpose of testing the performance of the inhibitor developed. At the same time these samples were analyzed for chloride, carbonate, sulphate, total hardness, pH, etc. The results of the analysis of these water samples are shown in Table VI. Corrosion and immersion tests and polarization measurements were made in all these samples (with and without inhibitor), and the results were found to be very satisfactory.

A follow-up trip was made in March of 1978. Mr. Fred Vahldiek of AFML was also visiting the facility at that time. A meeting was held between Mr. Mike Cawley of MacDill, Mr. Fred Vahldiek of AFML, and Dr. M. Khobaib of SRL to discuss the incorporation of the inhibitor and the overall operation of the rinse facility. The facility at that time was closed for some major pavement work on the runway. At this meeting, the idea of the automatic feeding of the inhibitor into the rinse tank was abandoned due to cost considerations and the difficulty in monitoring the concentration level of the inhibitor in the rinse tank. However, the need for some mixing unit was strongly felt. Several alternatives were discussed. A network of PVC piping with air holes provided at approximately 300-mm (12-in.) intervals to bubble the air was designed, and the

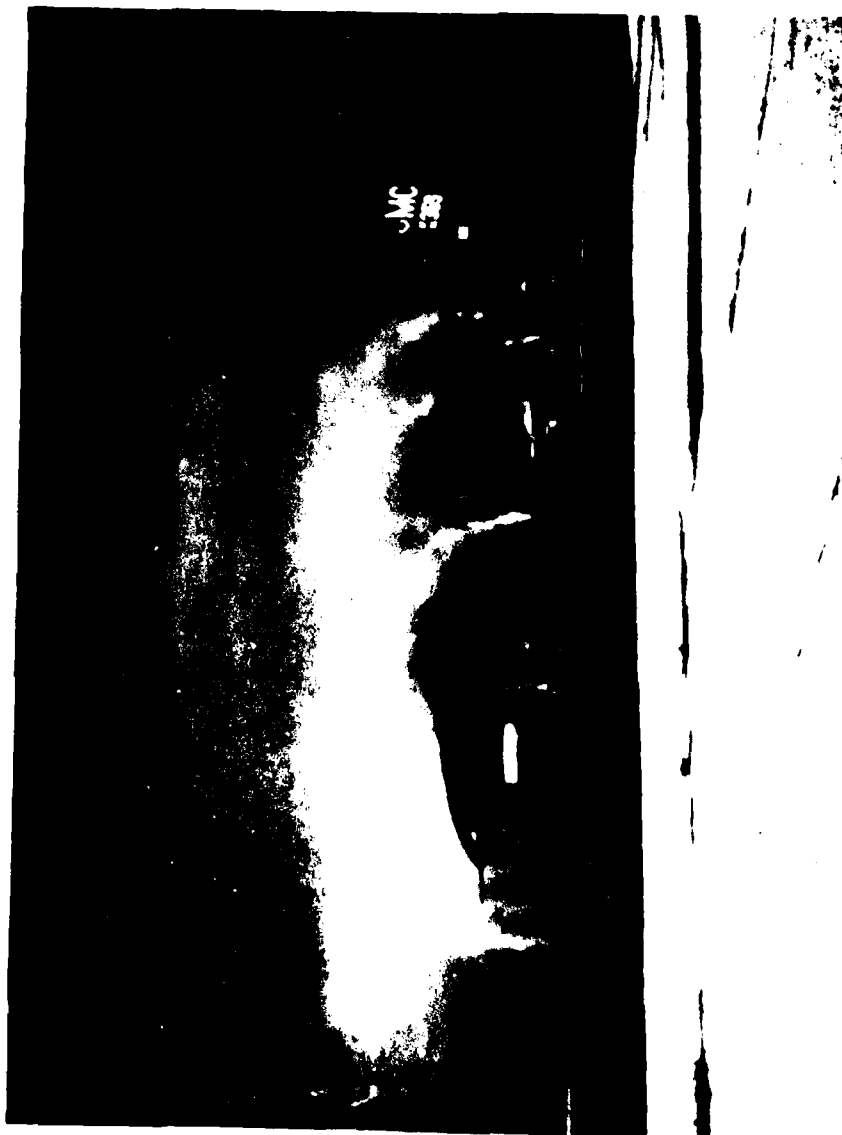


Figure 18. F-4 aircraft passing through the rinse facility

TABLE VI
ANALYSIS OF RINSE WATER, BEFORE AND AFTER RINSE

<u>Sample Identification</u>	<u>Fresh</u>	<u>After One Rinse</u>	<u>After Few Rinses</u>
Date Received by Lab:	10-7-77	10-7-77	10-7-77
Sulfates as Sulfur mg/l	38.39	25.03	30.04
Chloride, mg/l	10	15.33	2.473
Hardness as CaCO ₃ , mg/l	98	104	192
Alkalinity - Total as CaCO ₃ , mg/l	87	62	58
Calcium-Hardness, mg/l	110	73	43
Magnesium-Total, mg/l	4.5	50.0	3.5
Nitrates	0	0	0.255
Residual Chlorine	0	0	0

responsibility for having the unit fabricated and set up for proper operation was accepted by Mr. Mike Cawley at MacDill. An air compressor was inserted in the line to pass air continuously at nearly 3 psi.

With regard to the inhibitor, several chemical companies were contacted to obtain information on custom blending and packaging of the inhibitor formulation. Orders were placed with Erny Supply Company [5406 North 59th Street, Tampa, Florida 33610, phone (813) 621-3487] for custom blending, proper packaging (placed in a plastic bag, then sealed in a plastic pail), and shipping of the inhibitor to MacDill for use in the rinse facility. The approximate cost of the custom-blended, packed inhibitor is nearly \$.75/lb.

Another trip was made to MacDill in late August of 1978 to assist and supervise the incorporation of the inhibitor into the rinse tank. Dr. C. T. Lynch of AFML was also visiting the facility at that time for the same purpose. Dr. Lynch of AFML, Mr. Cawley of MacDill, and Dr. Khobaib of SRL worked as a team for three days to incorporate the inhibitor into the facility. The calculated amount of inhibitor was added to the tank, and the mixing of the inhibitor was carefully monitored. The mixing was achieved with the aid of an air compressor. The inhibitor was dissolved into solution within ten minutes without any difficulty. The washing operation was also very satisfactory. The aircraft structure (after the wash) and the metallic components at the rinse facility washed by the inhibited water were visually inspected for any trace of sedimentation. All surfaces appeared to be clear, and there was no sign of streaking caused by either undissolved inhibitor or precipitation out of the inhibitor.

A heavy-duty conductivity meter was installed in the tank to serve as the controller for the inhibitor-concentration level. The control circuit was designed and installed at MacDill. A calibration chart of the conductivity as a function of concentration of the inhibitor was prepared and cross checked at MacDill. This calibration chart is shown in Fig. 19.

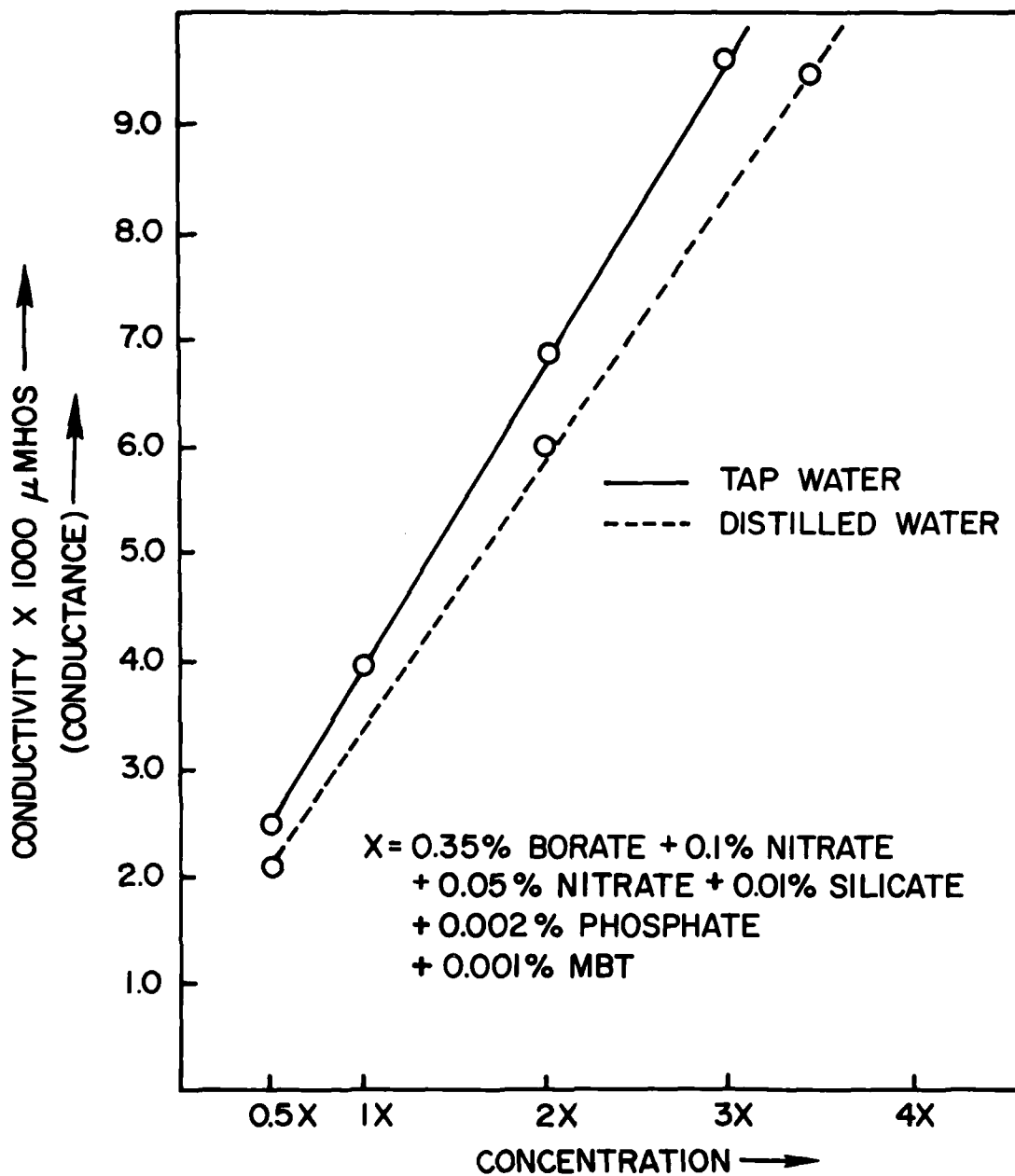


Figure 19. Calibration chart of conductivity as a function of concentration

A continuing series of visits was made to MacDill to insure optimum operations of the rinse facility. Mr. Walter Tripp of SRL visited the rinse facility to discuss the problem of monitoring the conductivity. A second conductivity meter and an automatic valve actuated by the conductivity meter were added to the main arrangement to control the flow of unwanted rain water from the runway. Operation of the rinse facility was fully satisfactory at the end of this project.

SECTION IV

RESULTS

Table V shows the results of some of the immersion tests conducted. Figures 20-26 show the anodic and cathodic polarization behavior of Al 7075-T6, Al 2024-T3, 4340 steel, and copper in different aqueous solutions. The crack-growth rates are plotted in Figs. 4-12. Selected fractographs of the crack-growth specimens are shown in Figs. 13-17. The static test results were highly irreproducible and, hence, are not included in this report.

1. IMMERSION TESTS

A formulation of sodium borate, sodium nitrate, sodium nitrite, sodium phosphate, sodium metasilicate, and sodium salt of MBT was found to be very effective in inhibiting the corrosion of aluminum, copper, iron, and their alloys. This solution performed extremely well even when these metals were galvanically coupled. The optimum concentration level was found to be 0.35% sodium borate, 0.05% sodium nitrite, 0.1% sodium nitrate, 0.01% sodium metasilicate pentahydrate, 20 ppm sodium meta-hexa phosphate, and 10 ppm MBT. When the concentration was doubled, good results were also achieved; however, after four to six weeks, some of the ingredients began to precipitate out. A lower concentration level was effective only for 10-15 days. Light discoloration of aluminum appeared after two weeks when the concentration was reduced by 50%. In general if the concentration is too dilute or too strong, the effectiveness decreases significantly. Among the commercial inhibitors, Nalco 39L showed promise and could be used as an alternative. However, the formulation described above demonstrated superior results--especially in the presence of chloride ions--and it costs less than the Nalco 39L. The other commercial inhibitors were not found to be satisfactory for this specific application.

2. POLARIZATION TESTS

The results of anodic polarization of Al 7075-T6 in WPAFB tap water, distilled water, 0.1M NaCl, the inhibitor (0.35% sodium borate, 0.05%

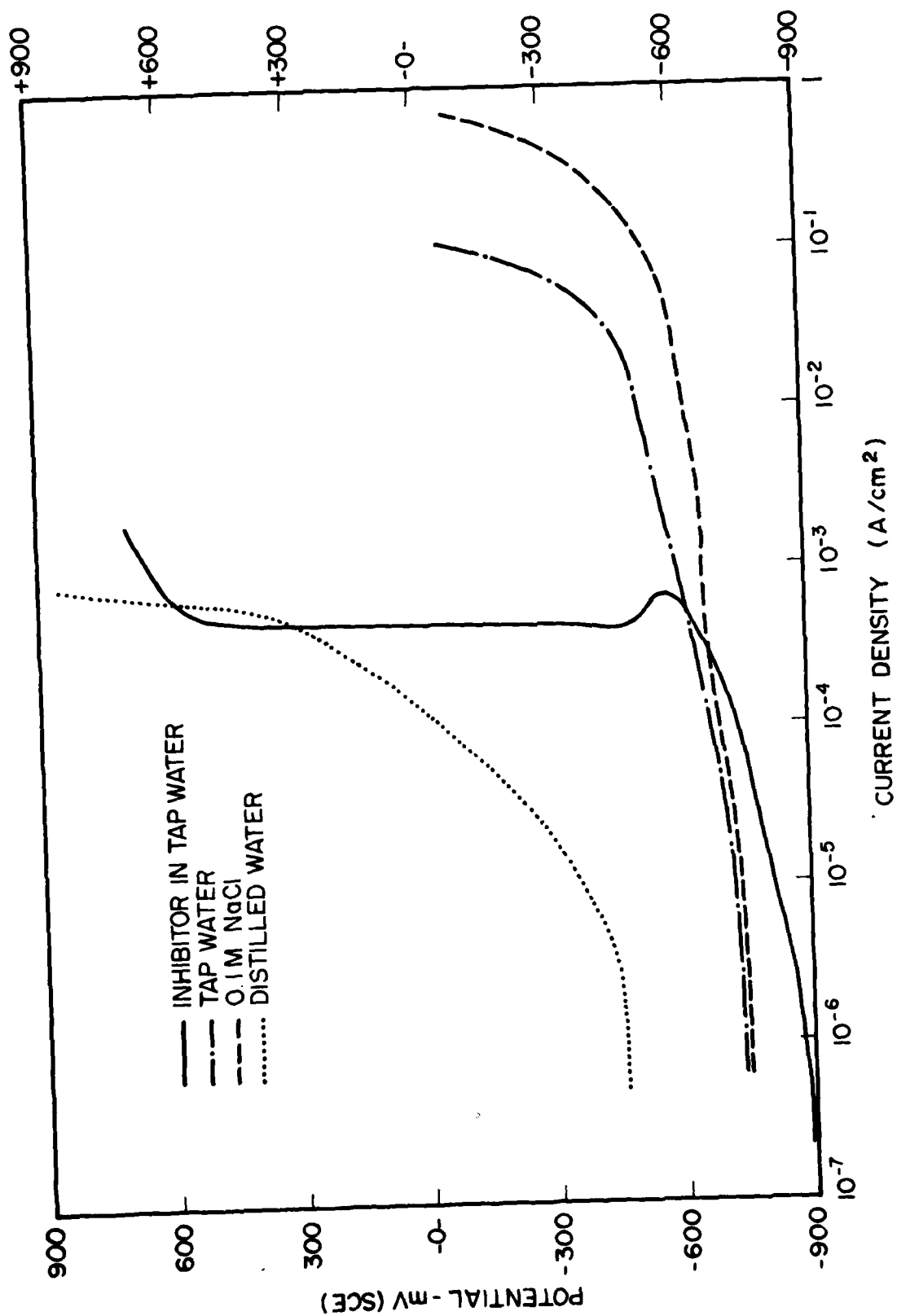


Figure 20. Anodic polarization of Al 7075-T6 in tap water, distilled water, 0.1M NaCl, and inhibitor solution

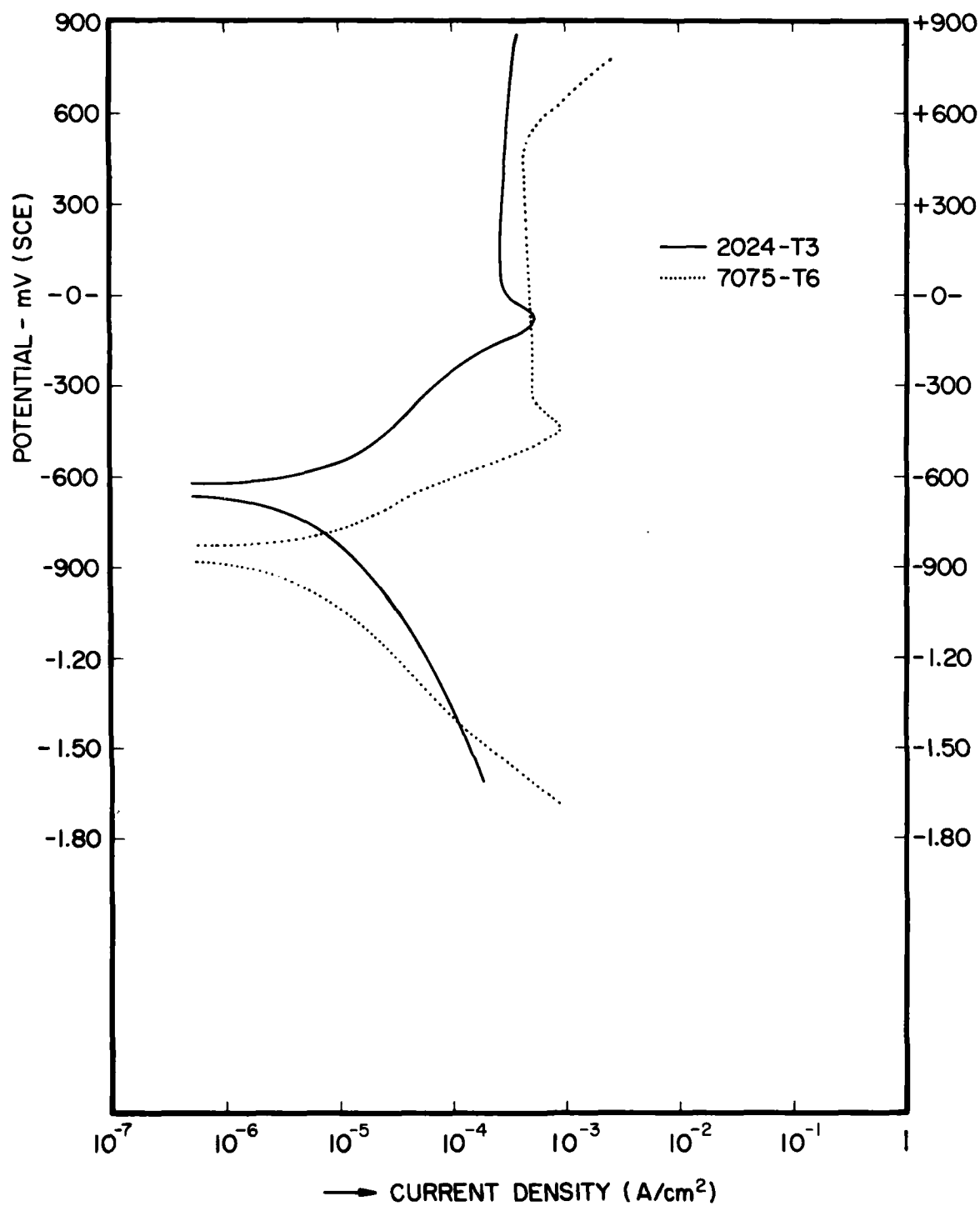


Figure 21. Anodic and cathodic polarization of Al 2024-T3 and Al 7075-T6 in an inhibited solution

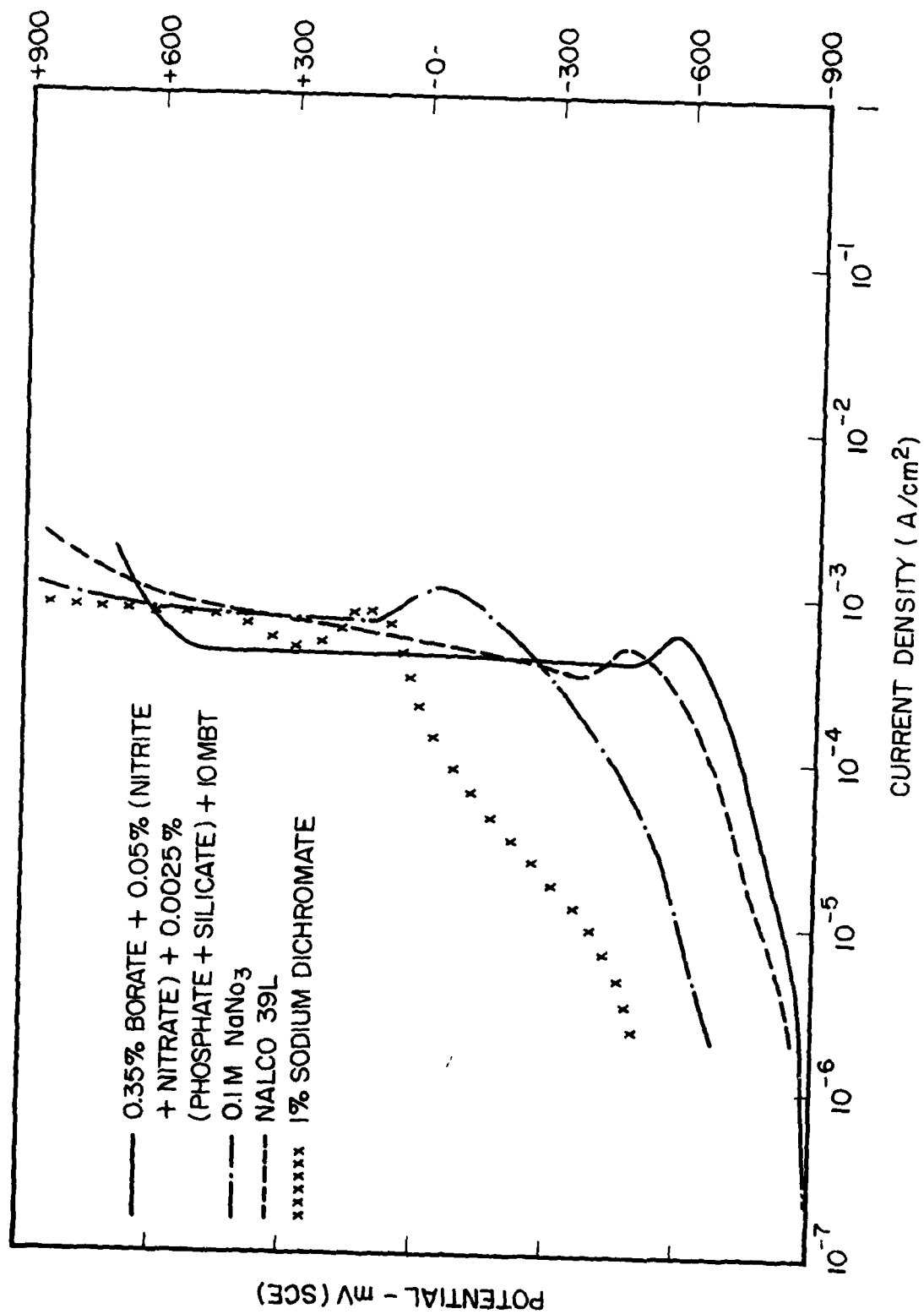


Figure 22. Polarization behavior of Al 7075-T6 in different inhibitors

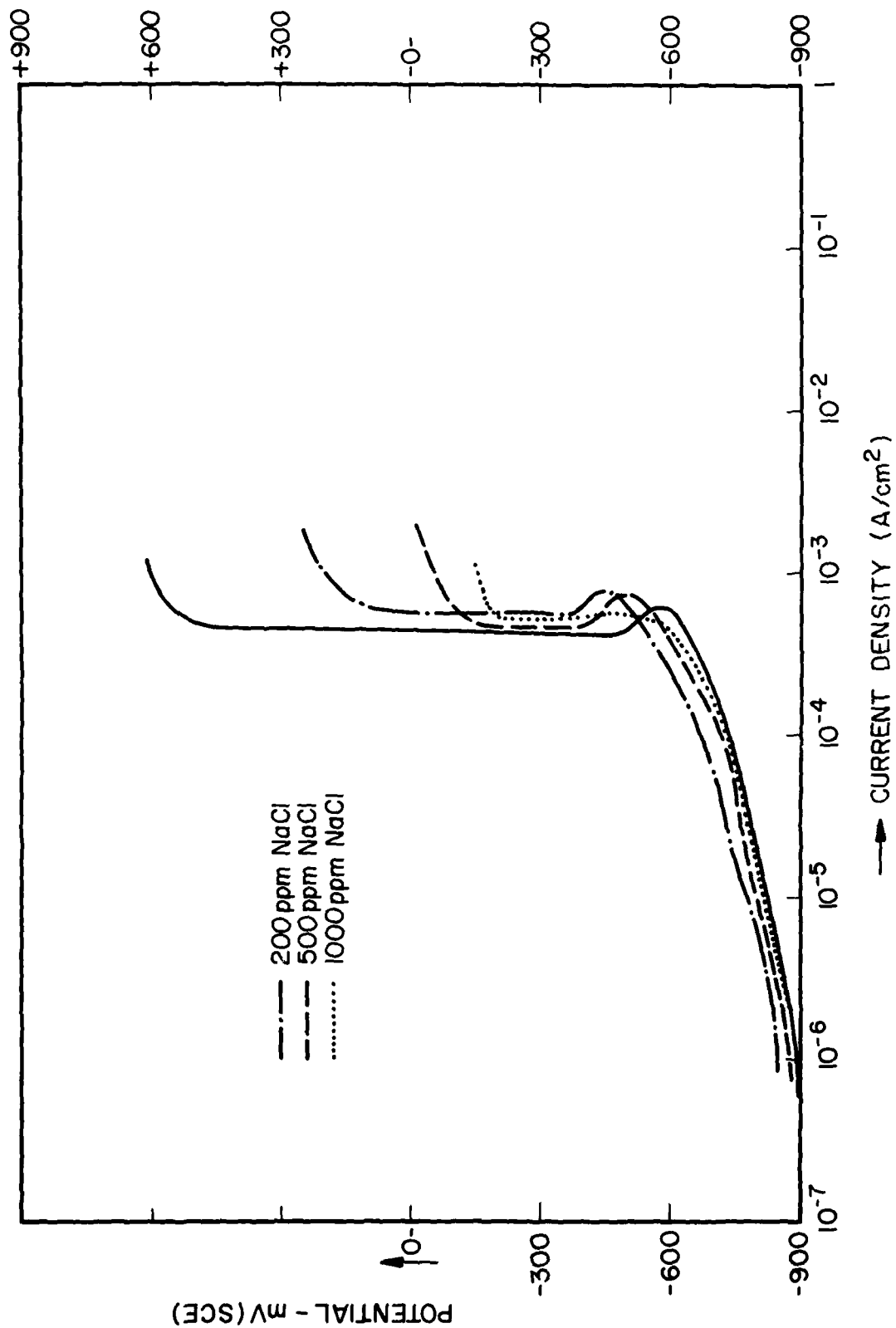


Figure 23. Effect of increasing chloride concentration upon the pitting behavior of Al 7075-T6 in an inhibited solution

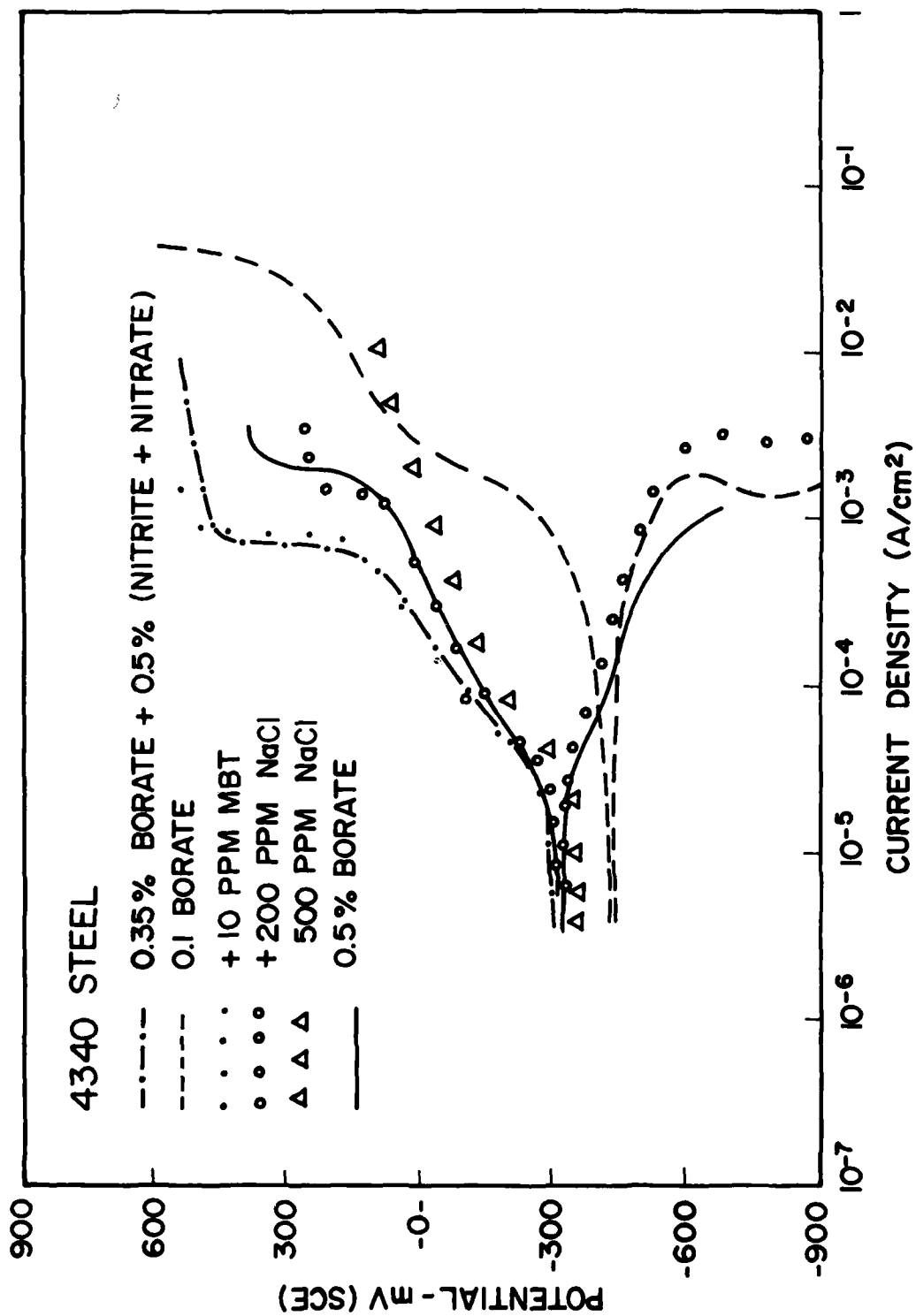


Figure 24. Polarization behavior of 4340 steel

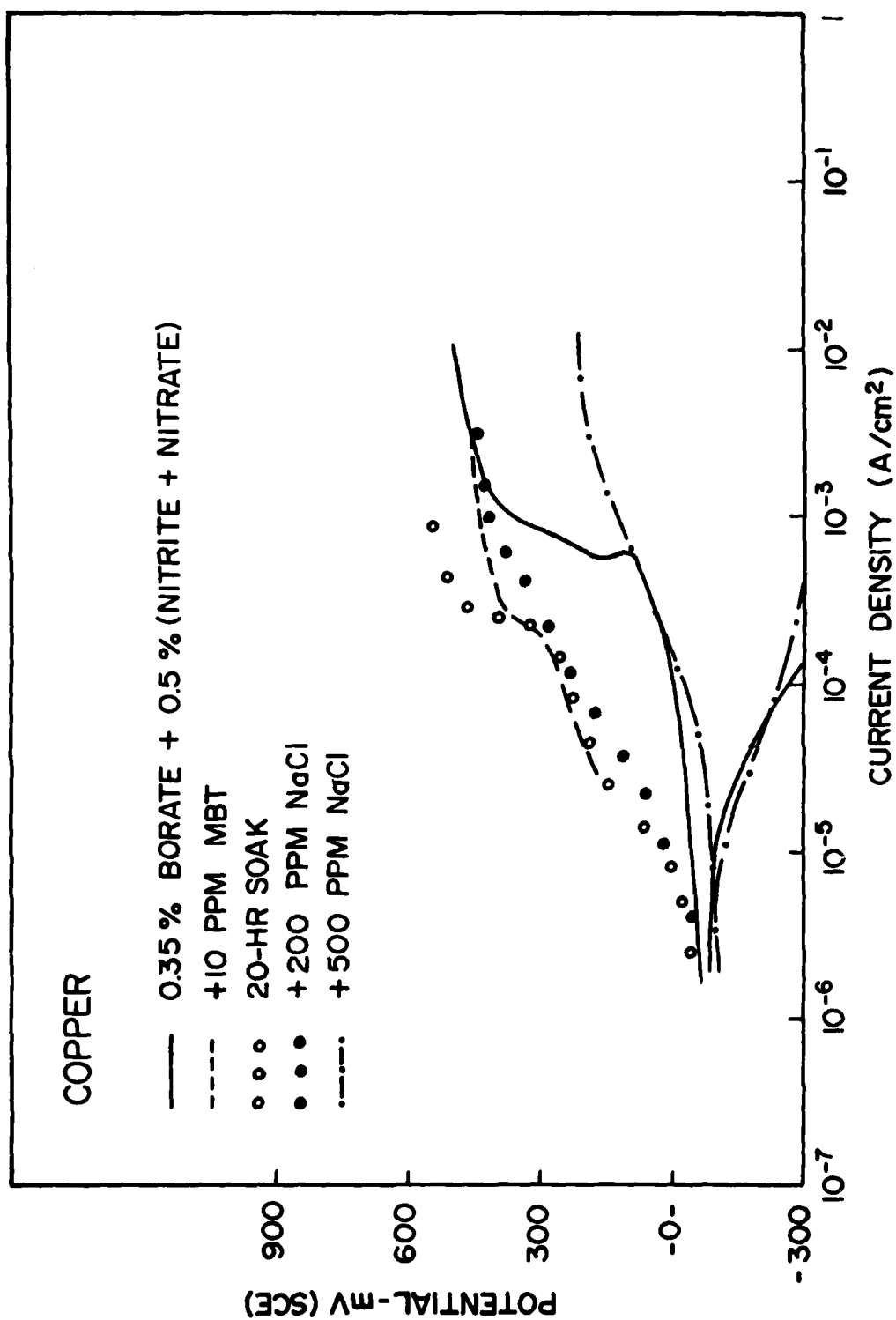


Figure 25. Polarization behavior of copper

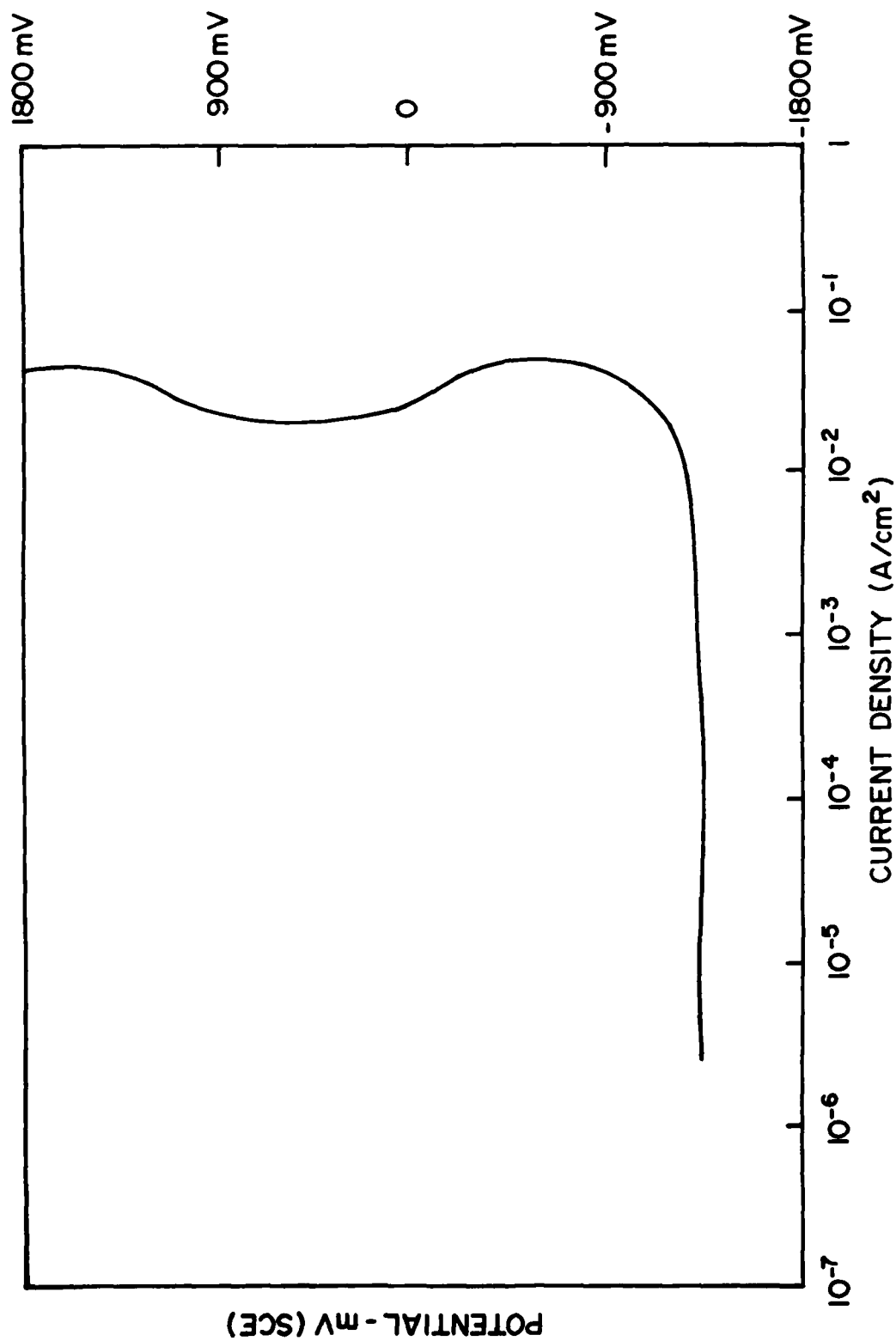


Figure 26. Polarization behavior of Al 7075-T6 in 1M Piperazine solution in distilled water

sodium nitrite, 0.1% sodium nitrate, 0.01% sodium metasilicate pentahydrate, 20 ppm sodium meta-hexa phosphate, and 10 ppm MBT) and Piperazine are shown in Figs. 20-26. Figures 20-21 show the anodic and cathodic polarization behavior of Al 7075-T6 and Al 2024-T3 in the inhibited solution. Some inhibitors which exhibited promising results are compared in Fig. 22 with the borate-nitrate based inhibitor. The performance of Nalco 39L was found to be satisfactory in these tests as well as in immersion tests. The effect of increasing the chloride-ion concentration upon the pitting behavior of Al 7075-T6 was also studied, and the results are shown in Fig. 23. Polarization tests with high-strength 4340 steel, cast iron, copper, and brass were conducted simultaneously. Some of these results are shown in Figs. 24 and 25 for 4340 steel and copper, respectively. The polarization data support the reported effectiveness of the inhibitor formulation in controlling the corrosion of steel, copper, and brass.

3. CORROSION FATIGUE

The low-cycle corrosion-fatigue results are shown in Figs. 4-12 for all the aluminum alloys tested. The crack-growth rate is lowest in ambient air, considerably accelerated in water (distilled or tap), and further accelerated by the addition of the chloride ion to the aqueous solution. Actually the crack-growth rate is more accelerated in Region I and is reduced nearly four to five times approaching Region II; and almost the same acceleration is maintained until fracture. Figure 5 shows the effect of addition of an inhibitor to the aqueous solution upon the crack-growth rate of Al 7075-T6 in the LT orientation. The reduction in the fatigue-crack-growth rate due to the addition of the borax-nitrite based inhibitor is clearly noticeable. The inhibitor addition reduces the fatigue-crack-growth rates from those observed in distilled water, tap water, and sodium chloride to that observed in ambient air. Figure 6 compares the effect of 1M sodium-nitrate addition and the borax-nitrite based inhibitor addition. The results are very similar--a small concentration of the borax-nitrite based inhibitor ($\approx 0.01M$) yields improved crack-growth retardation as compared to the 1M sodium-nitrate solution. If one compares the results of Figs. 4 and 6, the crack-growth rates in 0.1M NaCl for the T6 and T73 conditions are almost identical,

although T73 has been shown to be more resistant to SCC.¹⁴ Similar observations under corrosion-fatigue conditions have been reported by Jacko and Duquette.¹⁵

Figure 7 illustrates the corrosion-fatigue behavior of the same alloy, Al 7075-T6, which is stressed in the ST direction. The ST orientation in high-strength Al alloys is known to be more sensitive to stress-corrosion cracking and corrosion fatigue. The results are in agreement in the sense that the crack-growth rates are substantially accelerated in the 0.1M NaCl solution in the ST orientation as compared to the LT orientation, as can be clearly seen in Figs. 4 and 7. However, the effectiveness of the inhibitor can be easily observed, irrespective of orientation. Figure 8 shows the effect of an aggressive environment such as 0.1M NaCl upon Al 2024-T3 in the ST orientation. The effect of the inhibitor is similar to that with Al 7075-T6. The crack-growth rates are reduced in the air-sample level by the introduction of the inhibitor into the water.

A different experiment was performed to test the ability of this inhibitor in a situation involving a propagating crack. Crack growth was initiated in an aggressive solution of 0.1M NaCl and was allowed to reach the transition stage (from Region I to Region II). Then, the sodium-chloride solution was replaced by the inhibitor solution. The effect of this replacement upon crack growth is shown in Fig. 9. The experiment was repeated in the ST orientation. Here, the crack was initially allowed to grow to reach the apparent steady-state crack-growth value (Region II). The ability of the inhibitor to arrest and retard crack growth is shown in Fig. 10.

Striking results were obtained when an aqueous solution of 0.5M Piperazine zine was used as an inhibitor (see Fig. 11). The crack-growth rates were dramatically reduced as compared to those of the air sample. Apparently the K_{ICF} value was improved by more than 75% over that obtained in the ambient-air test. Verink¹⁷ and Das¹⁸ obtained very

promising results on crack-growth inhibition of high-strength steels by the introduction of 1M Piperazine. As a matter of fact, ΔK_{ICF} was improved nearly to the K_{IC} value in the presence of Piperazine and the fracture was fully ductile.¹⁸

4. SURFACE ANALYSIS

The results of analysis of some of the selected fractographs taken from the fracture surface of corrosion-fatigue-tested specimens are discussed here. Figure 13 is a fractograph of the ambient-air test sample in the vicinity of $11.8 \text{ mPa}\sqrt{\text{m}}$ ($13 \text{ ksi in.}^{1/2}$). Fatigue striations found across the entire surface are very smooth and ductile in nature, as can be seen in this figure.

In sodium chloride the fracture-surface features are somewhat different. Figures 13 and 14 are fractographs of an Al 7075-T3 sample tested in the stress-intensity $11.8 \text{ mPa}\sqrt{\text{m}}$ ($13 \text{ ksi in.}^{1/2}$) region. Figure 13 shows slip and large areas of cleavage on planes sharply inclined to the general fracture plane. Figure 14 is another definitive fractograph taken from the same sample, showing irregular fatigue striations as well as arrest markings caused by step-wise cleaving of the surface. As shown in Fig. 5, the addition of an inhibitor to the sodium chloride, distilled water, or tap water results in a decrease in the observed crack-growth rates. Correspondingly, the striation morphology is also affected. Figure 15 shows the striation morphology obtained from an inhibited solution. The striations are smooth and ductile in nature, being very similar to those resulting from the sample tested in air. Finally, Fig. 16 shows the features resulting from a sample tested in 0.1M NaCl, which was later replaced by an inhibited solution. This fractograph represents a transition region. The transition to a smooth and ductile striation morphology (resulting from the inhibitor solution) from brittle fracture features caused by the 0.1M NaCl solution is quite clearly shown here.

SECTION V

DISCUSSION OF RESULTS AND CONCLUSION

After a very intensive evaluation and development program, a multifunctional inhibitor consisting of borate, nitrite, nitrate, silicate, phosphate, and MBT was formulated. Nalco 39L was found to be satisfactory through the screening program, but the borate-nitrite based inhibitor proved to be more effective overall. The concentration of the mixture was optimized through polarization and immersion tests. Again, this formulation was found to be less sensitive to level of concentration than Nalco 39L. Nalco 39L at lower concentrations is not effective and, unfortunately, accelerates crack growth at higher concentrations. The borate-nitrite combination was found to be suitable up to a level of four times the optimized concentration.

As reported earlier, the higher concentration results only in precipitation out of supersaturated constituents--not loss of efficiency. At a lower concentration level, effectiveness decreases with time. Standard test coupons of high-strength Al, high-strength steel, copper, and brass immersed for more than six months in an inhibited solution showed no discoloration. The galvanic-couple tests also yielded excellent results. The polarization experiments showed reduction of two to three orders of magnitude in the corrosion current. The pitting experiments yielded good passivation results with the inhibitor, even in the presence of a chloride-ion concentration as high as 0.1%.

The corrosion-fatigue properties are also improved by this inhibitor. The results demonstrate the ability of the inhibitor to almost nullify the effect of an aggressive environment. One other inhibitor, namely Piperazine, was found to be far superior in this respect but was not found to be effective as a general corrosion inhibitor. Also it exhibited very low solubility in normal tap water. The fracture-surface analysis tends to indicate that most of the failures in the presence of the inhibitor are ductile. Even in the case of sodium-chloride solution, the brittle mode of fracture is transitioned to a ductile mode by the introduction of this inhibitor.

SECTION VI
NEW DIRECTIONS FOR RESEARCH

The development of a borate-nitrite based inhibitor and its effectiveness in controlling aqueous corrosion to the level of chromate suggests the need for further work. This inhibitor exhibits good potential for replacing chromate in most applications.

Piperazine has shown a more or less surprising property in aiding crack-growth retardation in high-strength Al alloys. The improvement to the apparent ΔK_{ICF} to K_{IC} value leads us to believe that Piperazine plays a wider role than simply one of annihilating the effect of environment. A detailed study on the mechanism of crack growth in an aqueous solution of Piperazine could resolve the argument concerning crack-tip blunting or formation of a thick passive film.

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